Synthesis of Silica Supported Iron Oxide (Fe_3O_4) Nanoparticles for Hexavalent Chromium Removal from Aqueous Solutions

By

Jibril Edris

A Thesis Submitted to

The Department of Applied Chemistry

School of Applied Natural Science

In Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry (Industrial Chemistry)

Office of Graduate Studies

Adama Science and Technology University

Adama Ethiopia

September 2018

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Declaration

I hereby declare that this M.Sc. thesis is my original work and has not been presented for a degree in any other university and all sources of material used for this thesis have been duly acknowledged.

Name: Jibril Edris

Signature: _____

This M.Sc. thesis has been submitted for examination with my approval as thesis advisor/ supervisor.

Major advisor	Co - Advisor
Prof. Neeraj K. Gupta	Dr. Eneyew Amare
_____	_____
Signature	Signature
Date of submission	Date of submision
_____	_____

Approval sheet

BY _____ _____ _____

Name of Student Signature Date

Approved by:

As thesis advisor, we hereby certify that we have read and evaluated this thesis paper under our guidance, by Jibril Edris entitled: **"Synthesis of Silica Supported Iron Oxide (Fe_3O_4) Nanoparticles for Hexavalent Chromium Removal from Aqueous Solutions"**. We recommended as fulfilling the thesis requirement.

_____ _____ _____

Major advisor Signature Date

_____ _____ _____

Co-advisor Signature Date

As members of the board of examiners for the M.Sc. thesis open defense examination, we certify that we have read and evaluated the thesis paper prepared by Jibril Edris and examined the candidate. We recommended the thesis paper to be accepted as fulfillment for the requirements of the thesis guideline of Adama Science and Technology University ⁄Applied Chemistry program

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Chair man Signature Date

_____ _____ _____

Internal Examiner Signature Date

_____ _____ _____

External Examiner Signature Date

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List of Abbreviations

AC	Activad Carbon
AOPs	Advanced oxidation process
CNTs	Carbon Nanotubes
DO	Dissolved oxygen
DW	Distilled water
EC	Electrocoagulation
ED	Electrodeposition/Electrodialysis
EF	Electrofloatation
FT-IR	Fourier Transforms Infrared
IONPs	Iron Oxide Nanoparticles
MCL	Maximum Contaminant Limit
MNPs	Magnetic Nanoparticles
NMs	Nanomaterials
NMOs	Nanomagnetic Oxides
NPs	Nanoparticles
nZVI	Nanozero Valent Iron
SPION	Superparamagnetic Iron Oxide Nanoparticles
XRD	X-Ray Diffraction

Abstract

Heavy metals in the environment are hazardous to human health and require better methods for detection and removal. Industrial effluent often contains significant amount of toxic hexavalent chromium (Cr(VI)). In this study, iron oxide (Fe_3O_4) nanoparticles were synthesized by chemical precipitation method using ferric chloride hexahydrate($FeCl_3.6H_2O$) and ferrous sulphate heptahydrate($FeSO_4.7H_2O$) as a precursors and sodium hydroxide (NaOH) and ammonium hydroxide(NH_4OH) as Precptating agent. To prevent excess aggregation of iron oxide nanoparticles silicon dioxide (SiO_2) was used as a supporting material. The obtained nanoparticles (unsupported and supported) were characterized by XRD and FT-IR spectroscopy analysis. The average crystallite size of the products were calculated for both unsuported and supported MNPs and were found to be 13.5 and 12.8nm respectively. The effect of different parameters such as pH, Cr(VI)concentration, adsorbent dose and contact time for efficiency of of Cr(VI) adsorption has been analyzed. The results showed that maximum Cr adsorption of 96.5% at pH levels of about 3. Optimum dosage of sorbent, chromium concentration and contact time were 0.7g, 20mg/l and 120min, respectively. Adsorption isotherms and kinetics were analyzed. The experimental data was analyzed by both the Langmuir and Freundlich models of adsorption. The adsorption isotherm data was fitted well to Langmuir isotherm. Results showed that the kinetic model of pseudo-first order provided a good description of the experimental data.

1 Introduction

1.1 Background

Water is the most essential compound on earth for human activities. Providing clean water is a primery requirement for both existence and better health (Pragnesh and Lakhan, 2014). Water pollution is increasing worldwide due to rapid increase of human population, domestic, agricultural and industrial activities which in tern are leading to life time threatening diseases (Schwarzenbach, *et al*., 2010).

Heavy metals are amonge the various life threatening pollutants, present in soil and aquatic bodies and endangering to health of humans (Duruibe, *et al*., 2007), animals(Boyd, 2010) and plants (Cheng, 2003). The global heavy metal concentration in various environments is increasing due to an increase in their use as well as number of industries. Most of the industrial wastewaters contain heavy metals such as cadmium(Cd), lead(Pb), zinc(Zn), arsenic(As), cobalt(Co) and chromium(Cr)(Duruibe, *et al*., 2007).

Among these heavy metals, Cr is considered as a factor which contaminates surface and mineral water. It mainly enters water as a result of industrial activities including electroplating, leather tanning, dying, mining, nuclear power plants effluents and photography chemicals (Smith and Ghiassi 2006). The most common forms of Cr found in water are Cr(III) and Cr(VI), which pose different environmental and health effects. Cr(III) is present in small amounts in food and is essential for metabolism in humans, plants and animals while Cr(VI) is highly toxic and is considered as strong carcinogenic, mutagenic and teratogenic which causes stomach pain, vomiting, severe diarrhea and bleeding (Cummings *et al*., 2007).

It is thus necessiry to remove such heavy metal from industrial water before it can be discharged into channels draining into the main aquatic bodies. A number of treatment methods for the removal of metal ions from aqueous solutions have been reported mainly reduction, ion exchange, solvent extraction, reverse osmosis, chemical precipitation, adsorption, biosorption and electro dialysis(Saha, *et al*.,2011). However all these methods have disadvantages such as production of large volumes of sludge, high cost of chemicals,

increased concentration of dissolved solids in the effluent, high startup costs and low efficiency (Mohammad, *et al*., 2015). In short, it may be said that the conventional methods for heavy metal ions removal are limited by technical and economic barriers, especially when the concentration of metals ions in the wastewater is low (<100 ppm) (Witek, *et al*., 2011). Therefore the search and development of an efficient and low cost removal processes is utmost important.

Adsorption is reorganized as an effective and economical process for a wide variety of applications, especially for the removal of heavy metals from wastewaters. The significant advantages of the sorption technique are its high efficiency in removing very low levels of heavy metals from dilute solutions, easy handling, high selectivity, lower operating cost, minimization of chemical or biological sludge, and regeneration of adsorbent (Ozdes *et al*., 2011). One of the most widely used adsorbents has been activated carbon, but it is quite expensive and, possibly, non-cost effective in the treatment of large waste water volumes (Nadeem *et al*., 2006). This is why alternative low-cost adsorbents are being paid considerable attention.

Amongst different developing adsorbent systems, the design and fabrication of nanoparticle-based adsorbents has generated great interest in a variety of scientific communities ranging from chemical, biological and environmental science to engineering. Nanoparticles have two key properties that make them attractive as sorbents: on a mass basis, they have much larger surface areas than bulk particles and their ability to be functionalized with various functional groups to increase their affinity towards target compounds (Saleh, 2017)

For high efficient removal of heavy metal ions from wastewater, nanoparticles must satisfy the following criterions (Theron, *et al*., 2005).

- the nanosorbents themselves should be nontoxic,
- the sorbents must show relatively high adsorption capacities to pollutants,
- the adsorbed pollutant should be removed from the surface of the nanoadsorbent easily
- the adsorbents should be infinitely recycled and

Recently, the use of nanosized magnetic material as adsorbents has attracted increasing interest due to their high surface area and unique superparamagnetism (Hanif and Shahzad, 2014). These properties lead to high adsorption efficiency, high removal rate of contaminants and easy and rapid separation of adsorbent from solution using magnetic field. The magnetic NPs are reusable after magnetic separation by removing the adsorbed toxic contaminants (Shen 2009).

Currently MNPs are used in wide range of applications, including shape selective catalysis, chromatographic separations, sorption of metal ions, enzyme encapsulation, in fields of biotechnology and biomedicine for applications such as cell labelling and separation, magnetic resonance imaging (MRI), enzyme and protein separations, targeted drug delivery and magnetic ferrous fluids hyperthermia. To date, many technologies, mainly co-precipitation (Mahdavian and Mirrahimi 2010), microemulsion (Drmota *et al*., 2012), thermal decomposition (Sharma and Jeevanandam 2012), hydrothermal synthesis (Xin 2012), microwave assisted (Ahmed 2013), sol-gel (Huang and Hu 2008) and sonochemical synthesis (Vijayakumar 2000) have been applied and reviewed for the production of these magnetic nanoparticles.

The stability of magnetic nanoparticles is utmost important for their applications and of primary interest are nanoparticles that can be prepared as stable colloids or isolated as powdered products. Agglomeration can occur at any stage during synthesis; e.g., aggregation and agglomeration of particles during precipitation is itself a subject of investigation (Bramley, *et al*., 1996).

The stability can be greatly improved by preventing their oxidation and aggregation. Modification of the surface of magnetic nanoparticles by attaching organic and/or inorganic materials is proven to greatly enhance the stability and this prevents aggregation. Further, these attached groups provide specific functionalities that can be selective for ion uptake. Surface functionalization can be done with organic materials such as amino groups, carboxyl acid, citric acid, oleic acid, silane, natural polymers (dextran, starch, chitosan, etc.), synthetic polymers (PVA, PAA, alginate, etc.) and inorganic materials such as silica, gold, silver, platinum, palladium, iron, carbon, metal oxides/metal sulphides(Wu, *et al*., 2008).

A good support should be cheap, widely available and able to disperse the metals to form feasible particle size. As an example, SiO_2 surface has been shown to strongly bind Fe (III) and Cr (III) via surface complexation (Oh *et al*., 2007) which may be important for Cr (VI) removal. Previous investigations have demonstrated that SiO_2 shell can prevent agglomeration and oxidation of nanoparticles including Fe_3O_4, and Fe (Li, *et al*., 2010). Also, nanoporous SiO_2 shell facilitates the mass transfer between Fe NPs and pollutant

This is due to its characteristics such as satisfying responsivity.

- low cytotoxicity
- high stability under acidic conditions
- inertness to redox reactions and
- easy to perform surface chemical modification.

1.2 Statement of the Problem

There has been growing concern over the diverse effects of heavy metals on humans, livestock and aquatic ecosystems. Wastewater from textile mills, tanneries, electroplating, galvanizing and other metallurgical industries, pigment and dyes manufacturing and paint industries and other metal processing and refining operations at both small and large scales contain significant amounts of toxic metal ions. These toxic metals and their ions are not only potential human health hazards but also to other life forms. Toxic metal ions cause physiological discomfort and at times life threatening illness including irreversible damage to crucial body systems. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems due to their toxicity. The problem associated with such ions pollution is that they are not biodegradable and are highly persistent in the environment. Thus, they can be accumulated in living tissues, causing various diseases and disorders. Their toxicity can result in reduced mental and central nervous functions, lower energy levels and damage to the blood composition, lungs, kidneys, liver and other vital organs.

Thus it is necessary to remove these metal ions from wastewater before it discharged. In this respect, various physicochemical remediation technologies have been developed for the removal of metal ions from aqueous media.

The design and synthesis of cost-effective nanoparticles(NPs) for environmental remediation, pollution detection and other applications has attracted considerable attention. Among these magnetic nanoparticles(MNPs) are of great interest due to their distinctive physical and chemical properties such as size effects, surface-to-volume ratio, interaction, magnetic adsorption separation (Ali *et al*., 2016). They not only possess efficient performance owing to high efficient specific surface area and absence of internal diffusion resistance compared to the traditional adsorbents but also may be recovered rapidly by application of external magnetic field (Nassar and Mater 2010).

The basic aim of the present work was to synthesize Unsupported Fe_3O_4 MNPs and SiO_2 supported MNPs(Fe_3O_4 MNPs-SiO_2) for use as adsorbents and to tes their Cr(VI) ion removal efficiency from aqueous solution. The Fe_3O_4 MNPs and Fe_3O_4 MNPs-SiO_2 were synthesized by the chemical coprecipitation method.

1.3 Objectives of the Study

1.3.1. General Objectives

The fundamental goal of this study was to synthesize a low cost and effective Nanoadsorbent based on Fe_3O_4NPs and with SiO_2 as support(Fe_3O_4NPs-SiO_2) for the removal of Cr(VI) ions from aqueous solutions.

1.3.2. Specific Objectives

- To synthesis silica supported IONPs.
- To Charecterize the synthesized IONPs by using XRD and FT-IR
- To determine optimum pH, adsorbent dose, Contact time and initial concentration of Cr(VI)
- To investigate and describe the batch kinetics of adsorption isotherm by different models

1.4 Significance of the Study

Various methods of treating industrial effluents containing heavy metals have been developed over the years. These methods have both advantages and disadvantages.

The significant disadvantages include high energy requirements, inefficient metal removal, generation of toxic sludge and expensive processing equipment. Therefore, there is a need to develop an efficient, rapid, cost-effective and environment friendly technologies for the removal of contaminants from water bodies. Among different technologies a simple, efficient, cost-effective and ecofriendly approach for removal of toxic metal ions in potable water, adsorption offers good flexibility in design and operation. Adsorption technologies are expected to generate high quality treated effluent water for safe and healthy use.

The recent worldwide trend to achieve higher environmental standards favors the usage of low cost systems for treatment of effluents. Concentration of adsorbate, extent of surface modification and adsorbent characteristics are the factors responsible for metal adsorption capability. Cost effectiveness and technical applicability are the two important key factors for selecting effective low cost adsorbent (Tripathi Ranjan 2015). In spite of the scarcity of consistent cost information due to variable expense of individual adsorbents dependent on the processing required and local availability, the widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended because of their local availability, technical feasibility, engineering applicability and cost effectiveness (Babel and Kurniawan 2003).

In this work, using iron salts as precursor(Fe source) and in a composite system by addition of SiO_2 as template or a support, Fe_3O_4NPs were prepared and evaluated as adsorbents for removal of Cr(VI) ions from aqueous solutions.

2. Literature Review

Environment is defined as a totality of circumstances surrounding an organism or a group of organisms especially, the combination of external physical conditions that affect and influence the growth, development and survival of organisms. It consists of the flora, fauna and the abiotic and includes the aquatic, terrestrial and atmospheric habitats (Gore 1997). The environment is considered in terms of the most tangible aspects like air, water and food and the less tangible, though no less important, the communities we live in. A pollutant is any substance in the environment which causes objectionable effects, impairing the welfare of the environment, reducing the quality of life and which may eventually cause death. Hence, environmental pollution is the presence of a pollutant in the environment; air, water and soil, which may be poisonous or toxic and will cause harm to living things in the polluted environment (Nagajyoti, *et al*., 2010).

The term heavy metals "refer to any metallic element that has a relatively high density and is toxic or poisonous even at low concentrations (Lenntech, 2004). Is a general collective term which applies to the group of metals and metalloids with atomic density greater than 4g/cm^{3}or 5 times or more than water (Hawkes, 1997). However, being a heavy metal has little to do with density but concerns chemical properties and the class includes Pb, Cd, Zn, Hg, As, Ag, Cr, Cu, Fe, and the platinum group elements (Duruibe, *et al*., 2007).

2.1. Sources of Heavy Metals

There are different sources of heavy metals in the environment. Heavy metal pollution can originate from both natural and anthropogenic sources. Activities such as mining and smelting operations and agriculture have contaminated extensive areas of world (Herawati *et al*., 2000). Heavy metals originate within the Earth's crust; hence their natural occurrence in soil is simply a product of weathering process.

Figure 2.1 depicts a snapshot of these different sources.

Natural	Agricultural	Industrial	Domesic	Miscellaneous
-Natural rocks -Volcanic eruption -Wind blown dust particles -Sea spray -aerosols	-Inorganic fertilizer -Pesticide -Sewage sludge & fly ash	-Industrial waste -Thermal power -Mining industry -Chemical industry -Variuos refineries	-e-waste -used batteries -inorganic and organic waste -used filters -biomass burning	-Incineration -Open dump -Traffic and other emission -Land fills -Medical waste
Gas/liquid/solid discharge of heavy metals from sources				

Figure 2.1 Different Sources of Heavy Metals (Srivastava, *et al*., 2017)

2.1.1 Natural Sources

Weathering of rock is considered the most significant contributor of heavy metals and the weathering process is influenced by the nature of the rock and the environmental conditions on which the concentration and composition of heavy metals largely depends (Abdu, *et al*., 2011). Materials of geologic origin have high concentrations of Mn, Cr, Co, Cu, Ni, Zn, Sn, Cd, Hg, and Pb. Volcanoes along with harmful and toxic gases are the high level emitters of Al, Zn, Mn, Pb, Ni, Cu, and Hg (Nagajyoti *et al*., 2010). The eruptions and wind blown dust particles are also the source of heavy metals. High concentration of Fe and low amount of Mn, Zn, Cr, Ni, and Pb occurs from wind-dust blowing from the desert region like the Sahara(Ross 1994). To some extent fire produces volatile heavy metals like Se and Hg which are part of carbonaceous matter (Naidu, *et al*., 1997). Natural vegetation contributes heavy metals to the environment through leaching, decomposition, and volatilization. Similarly, oceanic activities produce sea sprays and aerosols that contribute heavy metal into inland coastal areas (Monge, *et al*., 2015).

2.1.2 Agricultural Sources

Major contributors of heavy metals in agricultural soil are inorganic fertilizers that also include liming, irrigation waters and sewage sludge. Varying concentrations of Cd, Cr, Ni, Pb,

and Zn have been contributed by other sources, predominantly by fungicides, phosphate fertilizers and inorganic fertilizers (Tóth *et al*., 2016). Cadmium bioaccumulation in plants is of prime concern as it deposits on leaves at high concentration and that may be consumed by animals or humans. Sewage sludge, manure, limes is also the cause of cadmium enrichment (Niassy and Diarra 2012). High levels of major heavy metals are reached in agricultural soil (where concentration is generally low) by repeated use of phosphate fertilizer. Sewage sludge adds Cr, Cu, Zn, Pb, Ni, and Cd while animal manure augments the soil by adding Mn, Cu, Zn, and Co (Carnelo, *et al*., 1997). Land application of sewage sludge is one of the most important contributors of heavy metal in the soil (Sharma, *et al*., 2017). Several pesticides are also a major source of heavy metal contamination in agricultural fields (Marrugo, *et al*., 2017). Similarly, waste water irrigation is also a major contributor of heavy metal pollution (Islam, *et al*., 2017). Therefore, concentrations or amounts of heavy metals in agricultural soil depend on soil characteristics and the composition and application rate of inorganic fertilizers, pesticides, sewage sludge, and/or waste water.

2.1.3 Industrial Sources

Different industrial activities like mining and refinement are another major sources of heavy metal contamination (Figure 1). Mining activities emits various types of heavy metals which depend on the nature of mining practices used. For example, the use of Hg in gold mines has become a major contributor of this metal into the environment (Pavilonis, *et al*., 2017). Similarly, coal mines are the chief source of As, Cd, and Fe which can pollute adjacent soil. Vaporized heavy metals like Cu, Zn, Pb, As, Sn, and Cd combine with water and condense to form aerosols (Nagajyoti, *et al*., 2010). These may be either dry deposited (dispersed by winds) or wet deposited (precipitated in the form of rainfall) causing water and soil contamination. Similarly, waste run off from mines, dust from transportation of crude ores, corrosion and leaching of heavy metals also contaminate soil and water bodies (Rout, *et al*., 2013). Various refinery processes also contribute to heavy metal pollution in the soil. Heavy metals like B, Se, Cu, Zn, Cd, Ni, and Cs are emitted by petroleum industries, coal burning power stations, nuclear power stations and high tension wires (Zhu, *et al*., 2016). Another contributor of heavy metal pollution includes processing of plastic, paper, textiles, electronics, and wood preservation. Anti wear protectants for automobiles release Pb, Cd, Ni, Hg, Cr, and

Zn especially in inefficient engines. The combustion lead containing gasoline emits Pb in the atmosphere and incinerators for MSW produces a considerable amount of Zn, Pb, Al, Sn, Fe, and Cu.

2.1.4 Domestic Effluents

Effluents are most probably the largest contributor of the high concentration of metal found in ponds, lakes, and rivers (Singh and Kumar 2017). Effluents generally consist of (1)mechanically treated or untreated wastewater, (2)materials that have passed from the filters of biological treatment plants, and (3) waste material from sewage outfall which is discharged into water bodies like the sea. Urban runoff also presents a severe problem of heavy metal pollution.

2.1.5 Miscellaneous Sources

Other contributors of heavy metal pollution are comprised of refuse from incineration, industrial discharge, transportation or traffic emisssions and open dumps or landfills (Aryal, *et al*., 2017). Vehicular sources include Zn and Cd associated with dust from tire wear Cu and Cd from diesel engines and Cr, Ni and Zn from aerosol emissions (Chen *et al*., 2013).

2.2 Toxicological Aspects of Heavy Metals

Due to their mobility in aquatic ecosystems and their toxicity to higher life forms, heavy metals in surface and groundwater supplies have been prioritized as major inorganic contaminants in the environment. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural processes such as biomagnification, concentrations may become elevated to such an extent that they begin exhibiting toxic characteristics. These metals can either be detected in their elemental state, which implies that they are not subject to further biodegradative processes or bound in various salt complexes. In either instance, the metal ions cannot be mineralized. Apart from environmental issues, technological aspects of metal recovery from industrial waters need also be considered (Wyatt 1988).

Heavy metals disrupt metabolic functions of organism in two ways (Singh 2007).

1. they accumulate and thereby disrupt function in vital organs and glands such as the heart, brain, kidneys, bone liver, etc.
2. they displace the vital nutritional minerals from their original place, thereby, hindering their biological function.

It is however, impossible to live in an environment free of heavy metals. There are many ways by which these toxins can be introduced into both human and animal body such as consumption of foods, beverages, skin exposure and the inhaled air.

The danger of heavy metals is intensified by their almost indefinite persistence in the environment due to their absolute nature Hg, Pb, Cd, Cr (VI), Zn, As, Ni etc., are toxic heavy metals from ecotoxicoligal point of view (Gupta, *et al*., 2016). Table 2.1 shows Maximum Contaminant Level (MCL) standards for some heavy metals established by USEPA (Babel Kurniawan 2003).

Table 2.1 The MCL Standards for the Most Hazardous Heavy Metals (Babel and Kurniawan 2003)

Heavy Metal	**Toxicity**	**MCL(mg/l)**
As	skin manifestations, visceral cancers, vascular disease	0.050
Cd	kidney damage, renal disorder, human carcinogen	0.01
Cr	headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Cu	liver damage, Wilson disease, Insomnia	0.25
Ni	dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zn	depression, lethargy, neurological signs and increased thirst	0.80
Pb	damage the fetal brain, diseases of kidney, circulatory system and nervous system	0.006
Hg	disease of kidneys, circulatory and nervous system	0.00003

2.3. Heavy Metal Emissions

Heavy metals are emitted both in elemental and in compound (organic and inorganic) forms. Anthropogenic sources of emission are the various industrial point sources including former and present mining sites, foundries and smelters, combustion by-products and traffics (UNEP/GPA, 2006). Cr compounds are usually found in industrial purposes such as chromite ore mining, pigment production, tanning of leather, formation of wood preservatives and anticorrosive agents in cooking goods. Paint is a significant source of Cr(VI) but is still used for industrial applications (Kotaś Stasicka 2000). The salt form of Cr(III) and Cr(VI) compounds, called chromates are produced through mining, smelting, roasting and extraction. Chromates generate the toxic dust during manufactural processes. Several studies had investigated that toxicity about Cr dust in chromate production workers. Furthermore, industrial wastes from Cr manufacturing are known as significant source of the soil and water pollution (Garg, *et al*., 2007).

2.4 Treatment Techniques for Removal of Heavy Metals from Industrial Wastewaters

Many researchers have worked on developing efficient treatment technologies. Treatment technologies are mainly based on physicochemical, electrochemical or advanced oxidation processes. Physicochemical processes include membrane filtration, chemical precipitation, ion-exchange and adsorption. Electrocoagulation, electroflotation and electrodeposition are categorized under the name of electrochemical methods. Photocatalysis is one of the advanced oxidation processes. Beside all these, nanotechnology is a practical approach in treating wastewaters too. Among all these possible methods, those with cost-effective, environment-friendly and no further pollutants features are the favorites (Arezoo, *et al*., 2017).

On the other hand, there are biological processes such as the activated sludge process that are widely used in the treatment of industrial and municipal wastewaters and are mostly considered to be cheaper than physical and chemical methods. Biological processes are usually aimed at removing the readily biodegradable chemical oxygen demand (COD), or relatively

readily hydrolysable substances, but are not specifically designed to remove heavy metals (Dionisi 2014).

Figure 2.1 depicts a summary of the different methods used for wastewater treatment.

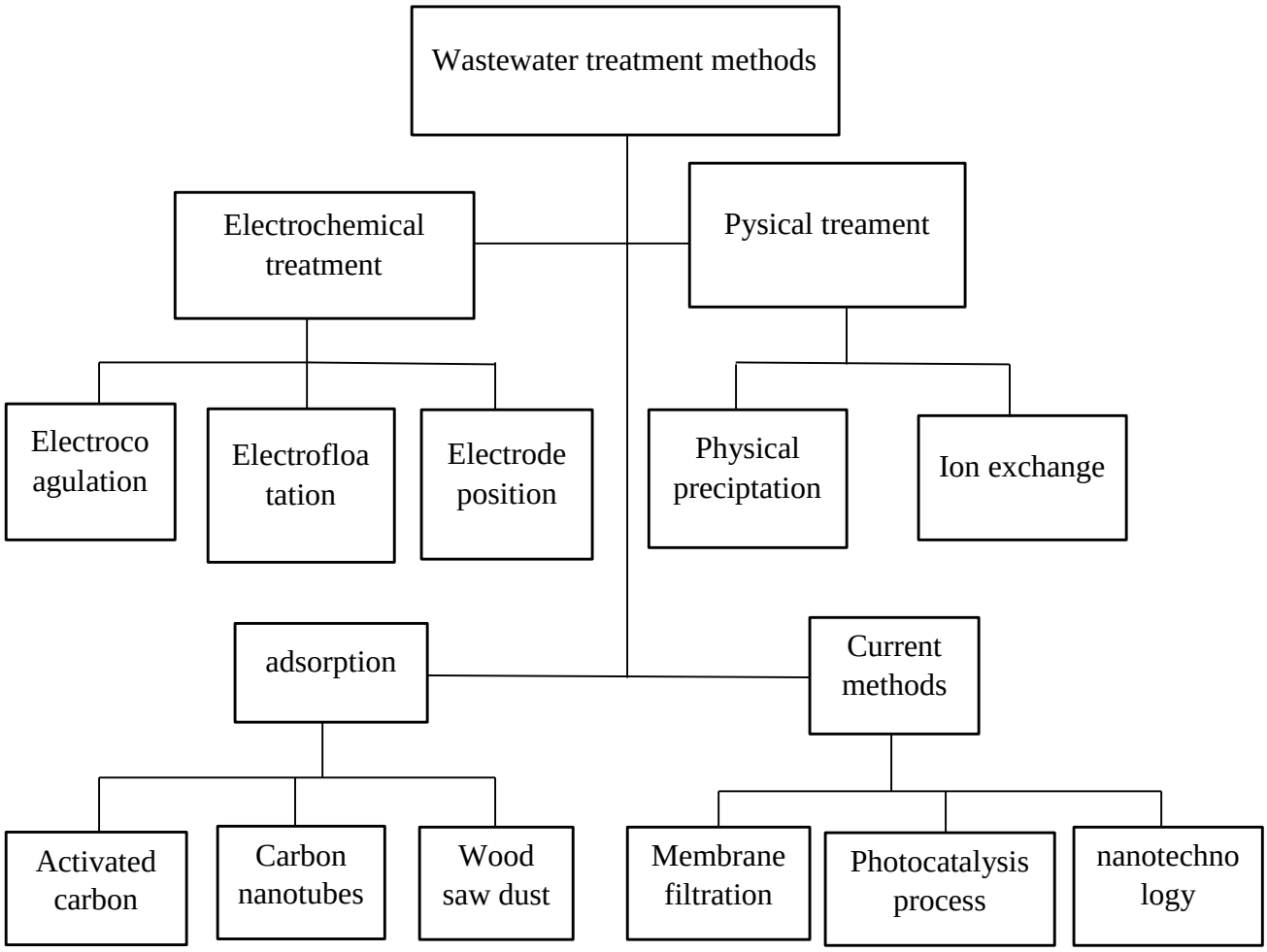


Figure 2.2 Tree Diagram for Wastewater Treatment Methods (Azimi, *et al*., 2017)

2.4.1 Conventional Methods for Wastewater Treatments

Electrochemical treatments of wastewaters have not received great attention so far because of the need of large capital investments and expensive electricity supply (Gupta and Ali 2013). The electrochemical technologies are in a situation that they are not only comparable with other technologies in terms of costs, but they also are more efficient and more compact. In some cases, the electrochemical technologies may be an essential step that cannot be neglected in treating wastewaters containing refractory pollutants (Khandegar and Saroha 2013).

2.4.1.1 Electrocoagulation (EC)

It is a simple and productive technology used in wastewater treatment industries (Emamjomeh and Sivakumar 2009) which recently became known as a small-scale wastewater treatment method with improved technical strategies (Khandegar and Saroha 2013). A wide variety of disturbing pollutants are removed by electrolysis (Jewel *et al*., 2007). In the process, treatment is done without adding any chemical coagulant or flocculant, thus reducing the amount of sludge that must be disposed (Cenkin and Belevstev 1985). A removal efficiency as high as 99% through EC has been reported for the treatment of oil wastes (Biswas and Lazarescu 1991), dye-containing solutions (Lin and Chen 1997), potablewater (Vik, *et al*., 1984), urban and restaurant wastewater (Chen, *et al*., 2000), nitrate or fluoride containing waters(Shen, *et al*., 2003) and treatment of heavy metal containing solutions (Jose, *et al*., 2005).

In the simplest form, the EC reactor is an electrolytic cell which has one anode and one cathode which are commonly known as sacrificial electrodes (Mohammad *et al*., 2004). These electrodes may be made of similar or different kinds of materials. Iron and aluminum are among the most popular materials (Jewel *et al*., 2007).

The procedure can be summarized as follows:

- Anode dissolution;
- OH^- and H_2 generation at the cathode
- Electrolytic reactions at electrode surfaces
- Coagulant adsorption on colloidal pollutants
- Colloids removal by sedimentation or flotation

As an example, when using Al electrodes, the main reactions include:

Anode: $Al \longleftrightarrow Al^{3+} + 3e^-$ .....(2.1)

Cathode: $3H_2O + 3e^- \longleftrightarrow \frac{3}{2}H_2 + 3OH^-$ .....(2.2)

Al^{3+} and OH^- ions formed at the electrode surfaces react in the wastewater:

$Al^{3+} + 3OH^- \longleftrightarrow Al(OH)_3$.....(2.3)

$Al(OH)_3$ acts as adsorbent and/or trap to separate heavy metal ions.

2.4.1.2 Electro-Floatation (EF)

Electroflotation(EF) has recently been applied to wastewater to remove heavy metal pollutants since other methods for treating wastewaters usually do not operate efficiently for very dilute solutions (concentrations below 50 mgm^{-3}) (da Mota *et al*., 2015).

EF became popular because of its adaptability, simplicity in design and operation, environmental compatibility, low running costs, and its small and compact units (Zodi *et al*., 2009). Because of its various features, EF can be used in a wide range of industries, e.g., treating oil from oil-water emulsions (Mostefa and Tir 2004), groundwater disinfection (Poon CP., 1997), apple juice and food processing effluents (Araya *et al*., 2008), colloidal and suspended particles (Fukui and Yuu 1985), swage water and pit waters (Il'in *et al*., 2002). EF separates pollutants by floating them to the surface of the liquid phase. The separation occurs through three basic parts. First, pollutants are attracted to a cell or reactor that has two electrodes and a power supply (Chen 2004). The overall reaction happening in the cell will be water electrolysis that releases oxygen and hydrogen into the solution:

$2HO_2 \longleftrightarrow O_2 + 2H_2$.....(2.4)

Heavy metals adhere or adsorb on the oxygen and hydrogen molecules whereby the emulsified particles will be destabilized and flocs will be formed. The second step is a separation for settling or flotation of generated foam and settled flocs. The third step is removing collected pollutants by filtration methods (Zodi *et al*., 2009).

To overcome the limitations of the EC and EF processes, some investigators combined EC and EF (electrocoagulation-flotation(ECF)) and have reported higher removal efficiency compared with using one alone. This combined method is a more safe and effective way to remove pollutants (Khandegar and Saroha 2013).

2.4.1.3 Electrodeposition (ED)

This is a practical and efficient method among the electrochemical processes for the recovery of heavy metals (Oztekin and Yazicigil 2006). Electrodeposition is advantageous because no

further reagents are necessary, no sludge is produced during the process, it is highly selective and low-cost as well (Chen and Lim 2005). It is a one-step clean method (Koparal *et al*., 2004) based on reduction and oxidation of heavy metal ions in a cell consisting of an anode, a cathode, an electrolyte cell and a current source (Sobha and Jayakrishnan 2012). The process transforms dissolved metal ions into solid particles by deposition on ionic conductors(cathode and anode) (Chen and Lim 2005) to protect them from corrosion(Koparal *et al*., 2004). Heavy metals are reduced and electroplated onto the cathode(Sobha and Jayakrishnan, 2012). The reaction is as follows:

$M^{n+} + ne^- \longleftrightarrow M$.....(2.5)

The final size and distribution of electrodeposits depends on the nucleation of deposits and their growth with the anodes preferred to be insoluble or inert(Sobha and Jayakrishnan, 2012), otherwise they will interfere with the recovery process of heavy metals.

A common side reaction at the anodes is (Chen and Lim 2005):

$4OH^- \longleftrightarrow O_2 + 2H_2O + 4e^-$.....(2.6)

Some competing reactions occur during the process. One of them is a reduction of H^+ into hydrogen gas:

$H^+ + e^- \longleftrightarrow \frac{1}{2} H_2$.....(2.7)

The efficiency of the whole process is influenced by the initial concentration of the waste solution, physical operational parameters such as temperature and pH and the presence of complexing and chelating agents(Jayakrishnan 2012). Electrodeposition is mainly used because it can be applied to non-aqueous solutions or solutions containing chelating agents as well. Either of these solutions yields better removal of a pollutant than aqueous solutions.

2.4.2 Physico-Chemical Processes

2.4.2.1 Chemical precipitation Techniques

Chemical precipitation is a simple, easily automated treatment method. This treatment method is widely used in removing heavy metals from wastewaters.

Chemical precipitation requires a lot of chemicals to reduce metal ions to an acceptable limit for discharge but it sometimes fails to reach this point (Özverdi, *et al*., 2006). These chemicals will be a large source of further pollution. In chemical precipitation processes, chemical precipitant agents react with heavy metal ions and change them into insoluble solid particles (Fenglian and Wang 2011). The solid phase will be separated from the solution by sedimentation or filtration (Matis and Kostas 2004). The reason that EC may be preferred to chemical precipitation is that EC doesn't need the addition of chemicals, leads to higher efficiencies, produces less sludge and removes species that chemical precipitation cannot remove (Khandegar and Saroha 2013). The adjustment of the pH is really important in this process; basic conditions with pH = 11 are preferred to improve the heavy metal removal. Chemical precipitation is effective and so far the most widely used process for metal removal from inorganic effluent. After pH adjustment to basic conditions (8-11), the dissolved metal ions are converted to insoluble solid phase via a chemical reaction particles (Fenglian and Wang 2011). The method changes the ionic equilibrium to form dissolved precipitates which can be simply separated by sedimentation.

2.4.2.1.1 Hydroxide precipitation

In this process, the incorporation of coagulants like iron salts, alum, and some polymers generally improves heavy metal separation from wastewater. Soluble metals can precipitate as hydroxide by filtration or sedimentation. Alkaline agents can be used to increase the pH of the water. Alkaline agents decrease the solubility of metal ions and therefore precipitate out of the solvent. The hydroxide precipitation reaction is (Gupta and Ali 2013):

$$M^{2+} + 2OH^{-} \longleftrightarrow M(OH)_2 \quad (2.8)$$

M^{2+} and OH^{-} represent the metal ions and the precipitant, respectively. $M(OH)_2$ is insoluble. When the pH is less than the optimum condition, a soluble metal complex forms:

$$M^{2+} + OH^{-} \longleftrightarrow M(OH)^{+} \quad (2.9)$$

$$M^{2+} + OH^{-} + nR \longleftrightarrow M(R)_nOH^{+} \quad (2.10)$$

The existence of organic radicals affects the hydroxide precipitation. A variety of chemicals are used as precipitants for chemical precipitation. The most common ones employed are lime and calcium hydroxide which are available in the most countries (Kurniawan *et al*., 2006).

Lime (CaO) is usually preferred to other precipitants, but a considerable high dosage is required and it may not be successful to reduce heavy metals to the standard limits due to inadequate settling and dissolution of precipitates (Chen *et al*., 2009).

2.4.2.1.2 Sulfide precipitation

The concept of sulfide precipitation is similar to hydroxide precipitation. Both soluble and insoluble can be used to precipitate metal ions. Sulfide is used to precipitate the heavy metal ions as metal sulfides and the sludge produced is removed from the solution by gravity settling or filtration. The sulfide precipitation process needs pre- and post-treatment and accurate control of reagent additions due to the toxicity of the sulfide ion and H_2S This precipitation method is conducted by tuning compositions and other circumstances so that the ionic constituents that are to be separated alter from a soluble ionic to a solid phase (Wang *et al*., 2005).

Compared with hydroxide precipitation, the solubility of the metal sulfide precipitates are dramatically lower, and hence the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range 7-11. Metal sulfide sludges also exhibits better thickening and dewatering characteristics than the corresponding metal hydroxide sludge (Fenglian and Wang 2011).

As an example, in an investigation of the use of pyrite and synthetic iron sulfide to remove Cu^{2+}, Cd^{2+} and Pb^{2+}, the mechanism governing the metal removal processes was determined as chemical precipitation at low pH (<3) due to H_2S generation Eqs. (2.11) and (2.12) and adsorption at high pH (3-6) (Özverdi and Erdem 2006).

$$FeS(s) + 2H^{+}(aq) \longleftrightarrow H_2S(g) + Fe^{2+}(aq) \quad (2.11)$$

$$2M^{n+}(aq) + nH_2S(g) \longleftrightarrow M_2Sn\,(s)\downarrow + 2nH^{+}(aq) \quad (2.12)$$

where M^{n+} and H_2S represent the dissolved metal ions and the precipitant, respectively, while M_2S *n* is the insoluble metal sulfide, and *n* is the coefficient of the reaction component, depending on the oxidation state of metal ions.

Recently, new sulfide precipitation process has been developed based on sulfate-reducing bacteria (SRB). SRB oxidize simple organic compounds under anaerobic conditions and the SRB transform the sulfates into H_2***S*** (Kousi, *et al*., 2007).

$$3SO_4^{2-} + 2CH_3CH(OH)COOH \longleftrightarrow 3H_2S + 6HCO_3^- \quad \text{.....(2.13)}$$

where $CH_3CH(OH)COOH$ stands for simple organic compounds. H_2S reacts with divalent soluble metals to form insoluble metal sulfides Eq. (2.13).

However, there are potential dangers in the use of sulfide precipitation process. As we know, heavy metal ions often in acid conditions and sulfide precipitants in acidic conditions can result in the evolution of toxic H_2S fumes. It is essential that this precipitation process be performed in a neutral or basic medium. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes.

2.4.2.2 Ion Exchange

Ion exchange treatment is based on a reversible interchange of ions between the solid and liquid phases (Kurniawan *et al*., 2006). The whole procedure begins with ion-exchange reactions, then the heavy metal ions will be physically absorbed, and a complex is formed between the counterion and the functional group. At the end, hydration occurs at the surface of the solution or pores of the adsorbent (Ferreira *et al*., 1999). Different factors such as pH, anions, temperature, the initial concentration of the adsorbent and sorbate, and time of contact affect the ion-exchange operation (Gode *et al*., 2006). In ion exchange, a reversible exchange of ions between the two phases (solid and liquid) occurs. In this method, a resin removes ions from an electrolytic solution and releases other ions of similar charge in a chemically equivalent amount and without any structural change of the resin occurring (Vineswaran *et al*., 2005).

Resins with acidic functional groups contain sulfonic acid in their structure; hence, it can be supposed that during metal ions capturing, the physicochemical interactions may take place:

$$nRSO_3^-H^+ + M^+ \longleftrightarrow nRSO_3^-M^{n+} + nH^+ \quad \text{.....(2.14)}$$

(resin) (solution) (resin) (solution)

where n refers to a constant of the reaction species, relating to the oxidation state of metal ions and $–RSO_3^–$ denotes the anionic group linked to the ion exchange resin (Dabrowski *et al*., 2004).

Ion exchange has a very specific place in treating wastewaters and removing heavy metals (Gode and Pehlivan 2003). When an ion-exchange cell with strong acidic cation exchangers is employed, heavy metals can be efficiently removed (Kang *et al*., 2004). It is usually preferred to other methods like chemical precipitation due to its high efficiency, low cost, less sludge volume, recovery of metals' value and high selectivity (Rengaraj, *et al*., 2001).

Among all the available kinds, synthetic polymer resins are pre preferred, such as styrene-divinylbenzene (Alyüz and Veli 2009). Another option are gel-like ones that are sometimes more efficient and cost less. Macropore resins have a sponge-like structure that provides better physical stability and leads to more stress relief (Gode and Pehlivan 2006).

Gel-like cation exchange resins like Lewatit S 100 are strongly acidic with beads of uniform size, e.g., it has been observed that this resin had a maximum ion-exchange capacity of 0.39 mmol $g^{–1}$ of Cr(III) under optimum conditions and pH=3.5 (Gode and Pehlivan 2006). Another resin Ambersep 132 is a strong basic resin with an adsorption capacity of about 92.10 mg $g^{–1}$ used to remove Cr(VI) (Lin and Kiang 2003). A cation exchange resin called IRN-77 helps to absorb the total amount of Cr(III) with an initial concentration of 100 mg $L^{–1}$ under the optimum pH of 3.5 (Rengaraj, *et al*., 2001).

2.4.2.3 Adsorption

Adsorption is a mass transfer process by which a substance (adsorbate) is transferred from the liquid or gas phase to the surface of a solid (adsorbent), and becomes bound by physical and/or chemical interactions (Kurniawan and Babel 2003).

It is now recognized as an effective and economic method for heavy metal treatment from wastewater and offers flexibility in design and operation and in many cases will produce high quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process (Fenglian and Wang 2011). A number of different metal-binding mechanisms have been postulated to be active in adsorption. According to the strength of the interaction adsorbate-adsorbent, these mechanisms can be divided into physisorptive and chemisorptive mechanisms where physisorption (e.g. physical adsorption and micro precipitation) is reacted by weak interactions such as London or Van Der Waals forces, while chemisorption (e.g. ion exchange, complexation, coordination and chelation) involves the net formation of chemical bonds adsorbent-adsorbate. Some examples of each are shown in Table 2.2.

Table 2.2 Differences Between Physiosorption and Chemisorption (Raj 2002)

Chemical Adsorption	**Physical Adsorption**
Chemical bonding is involved between adsorbates and the surface of the adsorbents	Intermolecular forces are involved between adsorbates and the surface of the adsorbents
Highly specific	Non specific
Monolayer	Can be both monolayer or multi-layer
Dissolution can occur	No dissociation of adsorbed
Can occur over a wide temperature range	Occurs at low temperature
Slow and is irreversible	Fast and the interaction is reversible
Bonds are formed as from electron transfer	No transfer of electrons

In general, there are three main steps involved in metal ions adsorption onto solid adsorbents: (i) the transport of the metal ions from the bulk solution to the adsorbent surface; (ii) adsorption of metal ions on the particle surface; and (iii) transport of metal ions within the adsorbent particle (María, *et al*., 2015). Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants (Verma and Khare 2014).

Adsorption processes have several advantages over the conventional methods of heavy metal removal. Some of the gains of adsorption process are: (I) economical, (II) metal selectivity, (III) regenerative, (IV) absence of toxic sludge generation (V) metal recovery and most importantly (VI) effective (Tripathi Ranjan 2015).

Adsorbents can be derived from agricultural waste, industrial by-products, or natural materials. Some of the most used adsorbents in this process are activated carbon (AC), carbon nanotubes (CNT), and sawdust.

2.4.2.3.1 Activated Carbon

Activated carbons(AC) are generally prepared from agriculture by-products when K_2CO_3 is used. However, any carbon-containing organic materials can be used to produce activated carbon. Its maximum surface area is in the range of 1266– 3256 m^2g^{-1} (Okada, *et al*., 2003). Adsorption by activated carbon is widely used for the removal of toxic metals and has been studied extensively (Abdel-Halim, *et al*., 2003). As an example, it has been shown that carbon prepared at 900 ^{0}C was more effective for removal of Ni(II) from aqueous solutions when the adsorbent concentration was 0.25g. The effect of the pH value on the adsorption was investigated and 100% Ni(II) removal was achieved in the range of pH 2–5, which are optimum pH values for cation adsorption (Erdoğan, *et al*., 2005).

Despite the high adsorptive capacity, the high costs of activated carbon and 10-15% loss during regeneration limit its global development. Moreover, activated carbon also shows high affinity towards organic molecules. As a result, these high molecular weight organic compounds will block the heavy metal ions from reaching the adsorbents bed. Due to these drawbacks, searching for alternative adsorbents is of extensive interest (Keng, *et al*., 2014).

2.4.2.3.2 Carbon Nanotubes

Carbon nanotubes(CNTs) are famous for their excellent properties and applications. Heavy metals sorbs to CNTs by a very complicated mechanism(Lijima, 1991). Some studies (Kabbashi, *et al*., 2009) showed that CNTs have a great potential for removing heavy metals. CNTs immobilized by calcium alginate (CNT/CA) reduce the risks caused by discharging a lot of CNTs into the water environment.

As an example, in seminal the work on Cu(II) absorption via CNTs and CNTs/CA, the results showed that at pH 5.0, 74.8% removal efficiency by using CNTs and 83.3% by using CNTs/ CA was achieved under experiment conditions (dosage of adsorbents: 0.05 g, concentration of Cu(II): 20 mg L^{-1})(Li *et al*., 2010).

2.4.2.3.3 Wood Sawdust

A solid waste product obtained from mechanical wood processing can be used as a low-cost adsorbent of heavy metals, largely due to its lignocellulosic composition. It is mainly composed of cellulose (45–50 %) and lignin (23–30 %), both with a capacity for binding metal cations due to hydroxyl, carboxylic and phenolic groups present in their structure (Šćiban, *et al*., 2007). Interest has risen recently in removing heavy metals from solution by binding with agricultural materials such as waste wool, nut wastes, tree barks, modified cotton and sawdust (Yu, *et al*., 2000). As an example, in a seminal work on the removal of heavy metals by sawdust, it was shown that the maximum removal efficiency observed for Cu(II), Zn(II) and Cd(II) were 76.2 %, 37.5 %, and 31.9% at 10, 20 and 20 g L^{-1}, respectively.

2.4.2.3.4 Natural Mineral Materials

As natural occurring minerals, zeolites have been widely applied in metal ion separation systems due to their valuable properties as cation-exchange capability. Among the most frequently used natural zeolites, clinoptilolite was shown to have high selectivity for certain metal ions such Cu(II), Pb(II), Cd(II) and Zn(II). Several clay minerals such as kaolinite clay (Jiang *et al*., 2010) and montmorillonite clay (Crini, 2006) were also proved to play an important role in metal ion removal by taking up cations either through ion exchange or physisorption or both.

2.4.3 Current Methods

2.4.3.1 Membrane Filtration Process

Filtration processes were developed and are used due to their higher removal efficiency, no pollution loads and sometimes lower energy consumption than conventional methods (Farno, *et al*., 2014).

Membrane processes are used in treating water and wastewater because of the simple separation method (Razavi, *et al*., 2016). This simple procedure is shared between different membrane processes with minor differences. In all processes, rejection is not achieved by flowing through the membrane physical pores, but due to a higher trans-membrane pressure (Sutherland, 2008), the separation occurs through a semi-permeable membranes with different pore size that make contact between desirable phases and control the passage of particles by letting solvent go and catching the solute (Sutherland, 2008).

These techniques include micro, ultra and nanofiltration and reverse osmosis. Molecules are separated based on the size of molecules by a sieving effect in micro- and ultrafiltration. In nanofiltration and reverse osmosis the interaction of membrane charge with ions of metals has a significant role in separation. Other driving forces are chemical, electrochemical and thermal, and concentration/vapor pressure gradients (Mulder, 1998).

Membrane separation technologies offer advantages over existing mass transfer processes (Lipnizki, *et al*., 1999).

- good removal of heavy metals
- high selectivity,
- low energy consumption,
- moderate cost to performance ratio and
- Compact and modular design

However, membrane processes have several inherent limitations. As examples, a membrane system designed to treat waste water may be limited by the water's osmotic pressure, viscosity, temperature and high concentration of suspended solids a major challenge facing widespread application of RO technology is membrane fouling, which results in reduced production capacity and increased operation costs. In practice, fouling reduces the permeate flux and can deteriorate the quality of permeate and therefore decreases membrane performance i.e. productivity, membrane lifetime and increases in operating pressure (energy) needed. All these things increase the costs of water treatment Therefore, many researches have been focused on enhancing the RO membrane resistance to fouling (Kang and Cao, 2012).

2.4.3.2 Electrodialysis (ED)

Electrodialysis(ED), a novel liquid hybrid membrane process (Sadyrbaeva, 2016), was developed by studies on desalination (Moon and Yun, 2014). It is used in the treatment of wastewater from different industries (Arribas *et al*., 2015) water splitting producing acid and base from salts (Moon and Yun 2014) as well as fractionation that includes wine stabilization, whey demineralization, etc.

ED has ion-selective exchange membranes (IEMs). IEMs do not transport cations and anions simultaneously. There are two kinds of these membranes: cation (CEM) and anion (AEM) exchange membranes (Arribas *et al*., 2015). Ion transportation through these membranes happens due to electrical potential or concentration gradient(Moon and Yun, 2014).

When the polarity of ED electrodes is reversed, the process is called electrodialysis reversal (EDR) which sometimes is better than ED. EDR lowers the scaling and fouling and has higher recovery rates(Arribas *et al*., 2015). But on the other hand, EDR needs more plumbing and electrical controls(Arribas *et al*., 2015).

2.4.3.3 Photocatalysis Process

Advanced oxidation processes(AOPs) are a relatively new technology in air and water purification industries(Litter, 2009). Photocatalysis is an AOP which uses nontoxic semi conductors that harness light with appropriate wavelength instead of chemical compounds and is preferred over chemical processes because of not using toxic materials as catalysts (Molinari, *et al*., 2015). The process became popular as an efficient process because of its simple design, low-cost operation, high stability and high removal efficiency (Jiang *et al*., 2012). While used in many industrial applications, it is powerful in eliminating pollutants such as heavy metals to protect the environment from contamination (Khalil, *et al*., 2002).

When a solution containing pollutants is introduced into a photocatalytic system, a five step process is conducted. First, the pollutants transfer to the surface from the aqueous phase. Second, they are then absorbed by the semiconductor surface. The third step are photocatalytic reactions occurring in the absorbed phase. Finally, the products are decomposed and removed from the interface region(Jiang et al., 2012). The major step of the treatment system is the

third one, where the photocatalysis processes occur. The whole process uses light as an activator. Therefore, the thermal activation of old processes is omitted (Herrmann, et al., 1993).

The photon excitation of the semiconductors is the initial step. When a light, especially visible light, with energy equal to or larger than the band gap energy of the semiconductor (not the pollutants) is illuminated, electrons from the valence band (VB) promote to the conduction band (CB). By this promotion, an electron-hole pair is created that leaves a photo-hole (h^+) in the VB and a photo-electron (e^-) in the CB, so in the light absorption process the following Eq. (2.15) takes place.

$$SC + hv \longrightarrow e^- + h^+ \quad \text{.....(2.15)}$$

At the same time, when electron-hole pairs are created, the reduction and oxidation of the pollutants takes place by exchanging photo-holes and photoelectrons according to Eqs.2.16 and 2.17. According to the redox potential of each pollutant, electron-holes proceed to the acceptor molecules and photo-holes transfer to the donor. After formation of ions in this phase, they react to form the intermediates and final products.

Reduction: $A + e^- \longrightarrow A^-$ .....(2.16)

Oxidation: $D + h^+ \longrightarrow D^+$ .....(2.17)

where A and D are pollutant species. Along these reactions, sometimes electron-hole recombination occurs according to Eq. 2.18. The process efficiency can be reduced by this reaction that degrades the photo-electric energy into heat (Mendive and Bahnemann 2011)

Recombination: $e^- + h^+ \longrightarrow$ heat.....(2.18)

Heavy metals can be eliminated by being deposited on the photocatalyst surface through the following reaction (Jin, *et al*., 2001):

$$M^{n+} + e^- \longrightarrow M \quad \text{.....(2.19)}$$

The deposition happens by the formation of small crystallites, whose size depends on the nature of the metal. This reaction transforms the ionic species into less toxic forms.

When the transformation is done, the recovery of the heavy metals by mechanical and thermal procedures is possible(Jin, *et al*., 2001). The following reactivity pattern was found under specific conditions Ag > Pd >Au > Pt >> Rh >> Ir >> Cu = Ni = Fe = 0 (Herrmann, *et al*., 1993)

Semiconductors that are used in photocatalysis are mostly of the chalcogenide type including oxides like TiO_2, ZnO, ZnO_2, CeO_2, WO_2, and sulfides like CdS, ZnS, WS_2, etc. (Litter, 2009). Despite the development of photocatalysis processes, they still face some limitations like recombination of electron or hole, producing unwanted byproducts, and the fault in absorbing visible lights.

2.4.3.4 Nanotechnology

Nanomaterials (NMs) are excellent adsorbents owing to their large surface area; therefore they are used widely in treating wastewaters containing heavy metals (Nogueira *et al*., 2015). It should be noticed that increasing use of nanoproducts and nano-adsorbents increase the risk of nano-pollutants in the environment (Gautam.*et al*., 2014).

Numerous studies (Xiaolei *et al*., 2013) have highlighted nanotechnology as a practical developing wastewater treatment system. The technology treatment systems overcome old major deficiencies and provide systems with higher removal efficiency, low waste generation, and specific uptake(Kar and Tewari, 2013). Generally, two major developing technologies are applied in treating wastewater solutions by nanomaterials; in situ and ex situ. In situ technologies are used when the wastewaters are treated in the place of contamination by injecting nano-sized particles whereas ex situ refer to treatments done after transferring the waste solution to a more convenient area. Whenever in situ technologies are feasible, they are preferred to ex situ, due to the cost effective features and higher removal (Kar and Tewari 2013). There are three kinds of nanoparticles: adsorptive, reactive and hybrid magnetic. Nano magnetic oxides (NMOs) are adsorptive nanomaterials. They are widely used in wastewater treatment systems due to their high surface area, stability, and the mesoporous structure (Kar and Tewari, 2013). The adsorption mechanism is based on the sequestration of heavy metal ions which leads to deep removal of heavy metals to reach the maximum contaminant limits (MCL) (Kar and Tewari, 2013). Adsorption efficiency obviously relies on physicochemical

conditions of the system and the chemical nature of the used absorbent (Kyzas and Matis, 2015).

Nano zero-valent iron (nZVI) is another nanoparticle used for wastewater treatment and heavy metal removal. It removes heavy metal ions by using reactive technologies, which make degradation and transformation of contaminants into harmless products possible(Ingle *et al*., 2014). In situ use of nZVI mostly begins by injecting it to the wastewater solution. It increases the ambient pH and decreases the redox potential of the solution. In addition to the changes applied to the wastewater after injecting the nZVI, the nZVI particles themselves undergo a chemical transformation by coating with natural organic matters in the waste solution(Grieger *et al*., 2010). The last kind of nanoparticles are hybrid magnetic nanoparticles (MNPs), called hybrid because they contain two or more nanometer-scaled components and magnetic because at least one component is magnetic (Zeng and Sun, 2008). They are widely used in a variety of applications not only because of their convenient magnetic properties, low-toxicity, and low price, but also because of a high surface-to-volume ratio which leads to a high adsorption capacity and high removal rates of contaminants (Singh *et al*., 2011). At diameters less than 20 nm, these particles have the maximum surface area and are in the supermagnetic state at room temperature (Hao *et al*., 2010). Among the magnetic nano-sized materials, iron oxides like magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) are the main representatives of MNPs (Digigow *et al*., 2014). Surface modification of MNPs to obtain more stabilized particles is essential (Carlos *et al*., 2013). There are various kinds of materials that can be used to coate MNPs, like polymer coating materials of lipids, poly(vinylpyrolidone)(PVP), poly(vinylalcohol) (PVA), etc.(Hao *et al*., 2010). The MNPs can be recovered and regenerated through a desorption process in a magnetic field (Gautam *et al*., 2014).

As an example,in a seminal work (Hu *et al*., 2007), various types of MNPs have been synthesized by chemical co-precipitation and used for the removal of Cr(VI) from synthetic electroplating wastewater. The Cr(VI) removal performances were compared and the adsorption capacities followed the order: $MnFe_2O_4$ > $MgFe_2O_4$ > $ZnFe_2O_4$ > $CuFe_2O_4$ > $NiFe_2O_4$ > $CoFe_2O_4$.

2.4.3.4.1 Superparamagnetic Iron Oxide Nanoparticles (SPION)

Magnetite is one of three types of iron oxide that exist in nature. Magnetite contains both Fe^{2+} and Fe^{3+} ions. It has the strongest magnetism compared to α-Fe_2O_3 and γ-Fe_2O_3 because its form is more stable (Cornell, *et al*., 2003). Magnetite, a classified as magnetic material, is dependent upon its magnetic susceptibility(χ). Moreover, iron oxide nanoparticles can be divided into magnetic classes: paramagnetism, ferromagnetism and superparamagnetism. Supermagnetism occurs when dipoles align themselves in a parallel orientation to an applied field. In the absence of the magnetic field, magnetite's direction is disorganized due to the thermal energy (Lu *et al*., 2007). The advantages of magnetic nanoparticles are the size of the particles that enhances the surface to volume ratio. The superparamagnetic properties are believed to be very suitable for the extraction of different types. In addition, magnetite nanoparticles can be easily separated and collected by applying an external magnetic field.

The chemical reaction that takes place during magnetite formation from iron salts solutions by Increasing the pH can be represented in the following overall chemical equation (Gnanaprakash et al., 2007):

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \quad (2.20)$$

In general, the solubility of trivalent iron oxide (Fe^{+3}) is smaller than the one observed on divalent iron oxides (Fe^{+2}). The trivalent iron hydrolyzes and forms hydroxide species. The hydrolysis can be induced by heating up the solution. The complete hydrolysis corresponds to the formation of a trivalent iron oxide-hydroxide and it is represented according to the following chemical reaction

$$Fe(OH)_3 \rightarrow FeOOH + H_2O \quad (2.21)$$

The divalent iron cation in solution (Fe^{+2}) reacts to form the divalent iron oxide in basic conditions (presence of hydroxyl ion OH^-), which is presented in Eq. 2.22

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (2.22)$$

Under the reaction conditions, divalent iron hydroxide and trivalent iron oxide-hydroxide species were likely to be formed. This being established, it is suggested that the following chemical reaction mechanism occurred: trivalent iron cation hydrolyzes forming (FeOOH) as pH increases; under alkaline conditions divalent iron cation forms $Fe(OH)_2$. Both chemical

species reacted to each other at pH values of around 8 to 12 forming magnetite according to Eq.2.23

$2FeOOH + Fe(OH)_2 \rightarrow Fe_3O_4\downarrow + 2H_2O$ .....(2.23)

Overall this is represented by Eq.2.24 (Mascolo et al., 2013):

$2Fe^{3+} + Fe^{2+} + 8OH^- \longrightarrow 2Fe(OH)_3 + Fe(OH)_2 \longrightarrow Fe_3O_4 + 4H_2O$.....(2.24)

Simultaneous hydrolysis and dehydration of Fe^{2+} and Fe^{3+} salts occurred during magnetite nanoparticle nucleation. Fe^{3+} ions immediately precipitated as ferrihydrite during hydrolysis at pH 3.0(Gnanaprakash et al., 2007). Fe^{2+} incorporates into ferrihydrite forming intermediate Fe^{2+} ferrihydrite complexes as pH increases. High electron mobility between Fe^{2+} and Fe^{3+} plays an important role in crystallization process. A small proportion of Fe^{2+} ions ($\geq$ 10 mol %) is essential to induce crystallization of all the iron into spinal magnetite nanoparticle structures (Gnanaprakash, et al., 2007).

3 Material and Methods

3.1 Materials

3.1.1 Chemicals

All chemicals used in this work were of analytical grade and procured through chemical traders in Addis Ababa. Ferric chloridehexahydrate ($FeCl_3.6H_2O$, 99%, Sigma Aldrich), ammonia solution (NH_4OH, 25%), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$, 98.8%, Sigma Aldrich), Siliconoxide(SiO_2, 45-60µm), distilled water and absolute ethanal (CH_3OH, 99.8%) were used for samples preparation, samples cleanup and further characterization and adsorption studies. For batch adsorption experiments, stock solutions of Cr(VI) were prepared by dissolving analytical grade of potassiumdichromate ($K_2Cr_2O_7$, 99.9%, Lobachemie, India) in distilled water and Diphenyl carbazide(98%, Lobachemie, India). Soduim hydroxide (NaOH, 99.8%, AR, Ranchem India) and hydrochloric acid (HCl, 35%, Riedel Dehaen, Germany) were used to adjust the pH of the solutions used for optimization experiments.

3.1.2 Apparatus and Equipment

3.1.2.1 Apparatus

Volumetric flasks(1000, 500, 250, 100, 50 and 25ml), graduated cylinder(100, 50, 10 and 5ml), beakers(1000, 500, 250ml) stoppered conical flasks (250ml), ceramic crucibles, glass rod are the apparatus used in this work.

3.1.2.2 Equipment

Instruments used in the present study included Fourier Transform Infra-red Spectrophotometer (FT-IR) (Model Spectrum 65 FT-IR Spectrometer, Perkin Elmer USA), X-ray Diffractometer (Model 7000S, Schimadzu Corporation, Japan), UV-Vis Sspectrophotometer (Model T 80+, PG Instruments Ltd., UK), and pH meter (Model pH 210, Hanna Instruments USA)

Other equipment included digital balance (Model ESj200–4, Masskot Scale, South Africa), orbital shaker (Model SK 300, GMI Inc., USA), centrifuge and laboratory oven.

3.2 Methods

3.2.1 Preparation of Fe_3O_4 NPs

The Fe_3O_4 NPs were synthesized by the coprecipitation method In a typical experiment, the stoichiometric ratio 1:2 between iron species, Fe^{2+}/Fe^{3+} was maintained. 6.0 g of $FeCl_3$ .6H2O and 3.0 g of $FeSO_4.7H_2O$ were dissolved in 100 ml distilled water under stirring for three minutes. The resulting solution was added in 25 ml NH_4OH 25% solution which was used as precipitant under vigorous stirring using a magnetic stirrer at 2000 rpm for about 30 min at temperature of 90 $^{\circ}$C. The pH was maintained between 8-12 by addition of NH_4OH dropwisely untill dark precipitate was formed(Figure 3.1a). The reaction mass separated into two phases on standing under the influence of a magnetic field: a clear aqueous phase on top and the consolidated precipitate at the bottom of the reaction vessel. This black colored precipitate was isolated by washinging repeatedly with distilled water and centrifuging to remove chloride and sulphate ions and NH_4OH until the supernatant become neutral (pH=7.0). The washed precipitate was then washed with ethanol and dried at 150 °C for 2h to obtain Fe_3O_4 NPs (Figure 3.1b).

3.2.2 Preparation of Silica Supported Fe_3O_4NPs (Fe_3O_4 NPs-SiO_2)

1.5ml (3mol/L) HCl solution was added into 13g/L SiO_2 suspension while stirring. Stirring was continued for 2h (This was to enhance the hydrophylic nature as well as to remove any metallic impurities) (Roche, 1999). After 2h, 50 mL serum was withdrawn and centrifuged. 6 g of $FeCl_3.6H_2O$ and 3g of $FeSO_4.7H_2O$ were dissolved in 50ml of 30:70 ethanol(CH_3CH_2OH) and deionized water (v/v) mixture and centrifuged. The acid washed SiO_2 (support material) was added to this solution while stirring at 2000 rpm. After 3 minutes 25ml NH_4OH 25% was added drop wise in 5-7 minutes as precipitating agent. Stirring was continued for a further 30 minutes at atemperature of 90 ºC and the pH was maintained between 8-12 by adding MH_4OH untill black colored precipitate was formed. The reaction mass separated into two phases on standing under the influence of a magnetic field. Clear aqueous phase on top and the consolidated precipitate at the bottom of the reaction vessel. The black precipitate was washed repeatedly by distilled water and centrifuging to remove NH_4OH until the pH of the supernatant become neutral (pH=7.0). The washed precipitate was then washed with ethanol

to remove water and dried at 150 ^{0}C for 2h to obtain Fe_3O_4 NPs-SiO_2 (Figure 3.1c). The procedure for synthesis of the Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 are summarized in the block diagram shown in figure 3.2

(a) (b) (c)

Figure 3.1 a) Black Colored Suspended Precipitate of Fe_3O_4 NPs; b) Oven Dried Fe_3O_4 NPs; c) Oven Dried Fe_3O_4 NPs-SiO_2

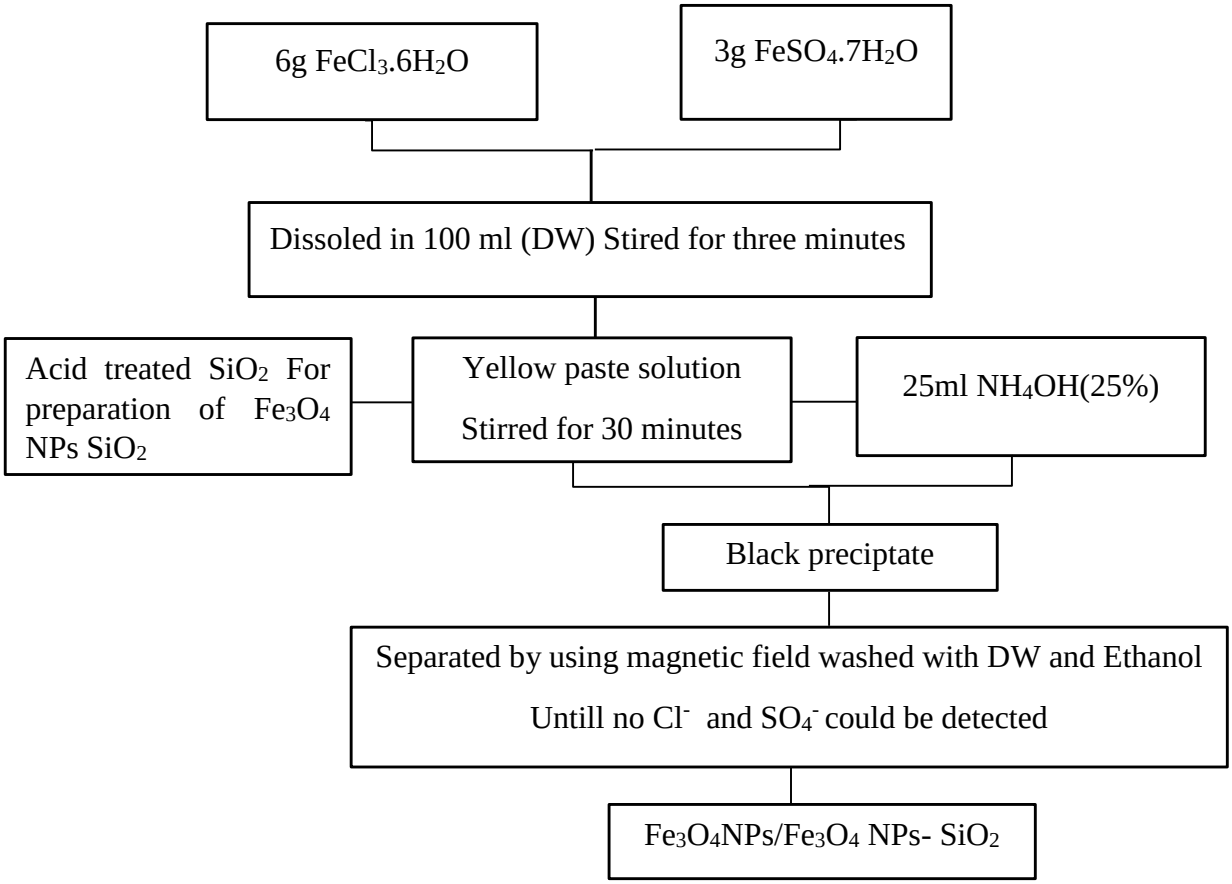


Figure 3.2 Block Diagram for the Synthesis Fe_3O_4 by Copericptation

3.2.3 Characterization Methods

3.2.3.1 X-Ray Diffraction Analysis (XRD)

XRD analysis to determine the crystal structures of the Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 samples was carried out at Adama Science and Technology University with CuKα radiation (λ=1.5406 Å) source with a nickel filter and continuous scan mode in the range $10^o < 2\theta < 80^o$.

3.2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The molecular characterizations of the Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 samples were carried out at the Department of Chemistry, Addis Ababa University College of Natural Science. Each sample of 1-2 mg was mixed with 100 mg KBr and pressed into disks at room temperature. The prepared KBr disks were scanned in the range 4000–400 cm^{-1} at a resolution of 4 cm^{-1} by the FTIR instrument equipped with a deuterium triglycine sulfate (DTGS) detector.

3.3 Preparation of $K_2Cr_2O_7$ Stock Solution and Standard Solutions

The standard stock solution of $K_2Cr_2O_7$ (1000 mg/L) was prepared by dissolving 2.828g of 99.9 % analytical grade $K_2Cr_2O_7$ in 1000 ml of distilled water. Standard working solutions of $K_2Cr_2O_7$ with different concentrations were prepared from the stock solution by appropriate dilutions. 20 mg/L, 40 mg/L, 60 mg/L and 80 mg/L of $K_2Cr_2O_7$ standard solutions were prepared by diluting 20 ml, 40 ml, 60 ml and 80 ml from the stock solution with distilled water in 1000 ml volumetric flasks upto the calibration mark respectively. The pH of the aqueous solutions was adjusted to the desired value byaddition of 0.1 M HCl or 0.1M NaOH solutions.

3.4 Adsorpton Experiments

A set of 250 ml conical flaks were covered with aluminum foil. To each conical flasks, 50 ml Cr(VI) solution and a certain amount of IONPs (0.1g-0.8 g) were added and the pH is adjusted by using 0.1M NaOH and 0.1M HCl. Then the solutions were shacked at 100 rpm for a required period of time at room temperature. The adsorbent was separated from the aqueous solution by using filteration.

3.5 Optimization of the Adsorption Conditions

The parameters initial chromium ion concentration, pH, contact time and sorbent dosage were chosen as independent variables and the removal efficiency of chromium is output response. The effect of various parameters such as contact time (30, 45, 60, 90, 120 and 150 min), pH (2, 3, 4, 5, 6, 7, 8, 9 and 10), adsorbent dosage (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 g) and initial metal concentration (10, 20, 40, 60 and 80 mg/L) were studied in term of their effect on reaction processes.

3.6 Adsorption Isotherm and Kinetic Studies

3.6.1 Adsorption Isotherm

Adsorption isotherm is defined as agraphical representation showing the relation ship between the amount adsorbed by a unit weight of adsorbent and the amount of adsorbate remaining in a test medium at equilibrium and it shows the distribution of adsorbable solute between the liquid and solid phases at various equilibriums. The isotherm results were analyzed using the Langmuir and Freundlich isotherm models.

3.6.2 Adsorption kinetic

Adsorption kinetics is performed to evaluate both the equilibrium time and the rate of Cr(VI) adsorption. The equilibrium time is one of the important parameters for subsequent adsorption isotherm studies. To evaluate the rate of Cr(VI) adsorption on adsorbents, the experimental data were analyzed using pseudo first and pseudo second order kinetic models. The pseudo second order model has been commonly used to describe chemical adsorption process of pollutants from aqueous solutions. Linear regressions were frequently used to determine the best fitting kinetic models and the method of least squares was used for finding parameters of the kinetic models.

3.7 Desorption Experiments

The experiments for desorption efficiency were carried out with dilute solutions of NaOH, KOH, HNO_3 and HCl. The agitation was performed on the orbital shaker for 90min. The metal ions concentrations were measured with atomic absorption.The desorption efficiency (DE) was determined using the following

$$DE = \frac{C \times V}{q \times m} \times 100 \quad \text{.....3.1}$$

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

4. Result and Discussion

4.1 Fe_3O_4 NPs Formation

Chemical co-precipitation consists in the precipitation of divalent (Fe^{+2}) and trivalent (Fe^{+3}) iron salts in an alkaline medium, maintaining a molar ratio of 1:2 by using NH_4OH to increase the reaction pH that is required to magnetite formation. Commonly the addition of alkaline solution to divalent and trivalent iron solution is made slowly, drop by drop (titration) under vigorous agitation using a magnetic agitator. The initial solution of divalent and trivalent iron cations had acidic pH 3-5 and after the titration is close to 8-12, a black precipitate is formed which indicates that the reaction has been completed.

4.2 Structural and Particle Characterization

Figures 4.2a and b show the XRD patterns of the Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 adsorbents. In both patterns, the diffraction peaks for Fe_3O_4 indicate that the formation of other compounds are absent. The diffraction patterns have well defined peaks which indicates that the samples are crystalline. Patterns of iron oxides and oxyhydroxide products of the JCPDS database are included for comparison (Figure 4.2) (Yamaura *et al*., 2004). Both magnetite and maghemite have a spinel structure. Their lines are close and it is difficult to distinguish them from one another by X-ray diffraction pattern. The absence of lines 110 (d = 4.183Å) at 2θ = 21.22° and 104 (d = 2.700Å) at 2θ = 33.15° indicates that both goethite (α-FeOOH) and hematite (α-Fe_2O_3) were not formed. Peaks of $Fe(OH)_3$ (d = 3.376 Å) at 2θ = 26.38° as well as other phases of iron oxide hydroxides, γ-FeO(OH) and δ-FeO(OH) (not shown in Figure 4.2) are not detected. As shown by the comparisons of Figures 4.1 and 4.2, magnetite constituted the dominant phase in both the Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 powders. The co-precipitation of maghemite is excluded by the absence of the (210) and the (110) peaks, which in the case of maghemite are present and at slightly higher intensities than the (111) peak, although trace amounts of maghemite may probably have formed as contaminants during the coprecipitation processes. Maghemite is brown, very different from black magnetite, but when present in trace amounts in a magnetite sample it is impossible to distinguish it by color. A series of characteristic peaks observed in the XRD patterns (Figures 4.2a and b) at 2θ of 30.2°, 35.5°, 43.2°, 53.6°, 57.3° and 63° corresponding to the diffractions of the XRD peaks are

indexed as (220), (311), (400), (422), (440), and (511) crystal planes, corresponding to a cubic unit cell of magnetite and they match the inverse-spinel structure of magnetite (space group of Fd3m, JCPDS Card no.79-0417) (Kushwaha *et al*., 2014). The diffraction peaks of Fe_3O_4 NPs-SiO_2 are broader than those of Fe_3O_4 NPs, indicating the finer nature and smaller crystallite sizes of the particles.

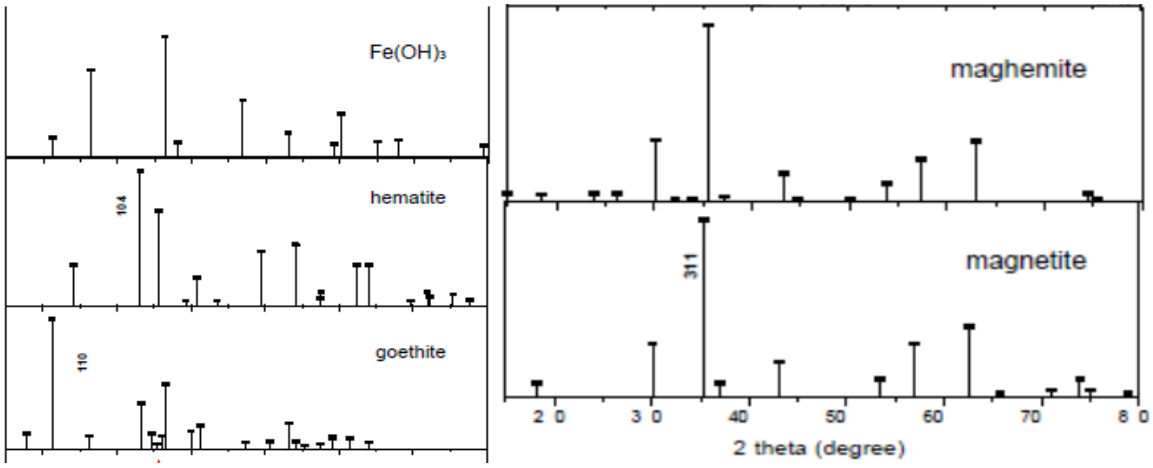


Figure 4.1 X-ray Powder Diffraction Patterns of Oxides and Oxyhydroxides from the JCPDS ICDD Database (Yamaura *et al*., 2004)

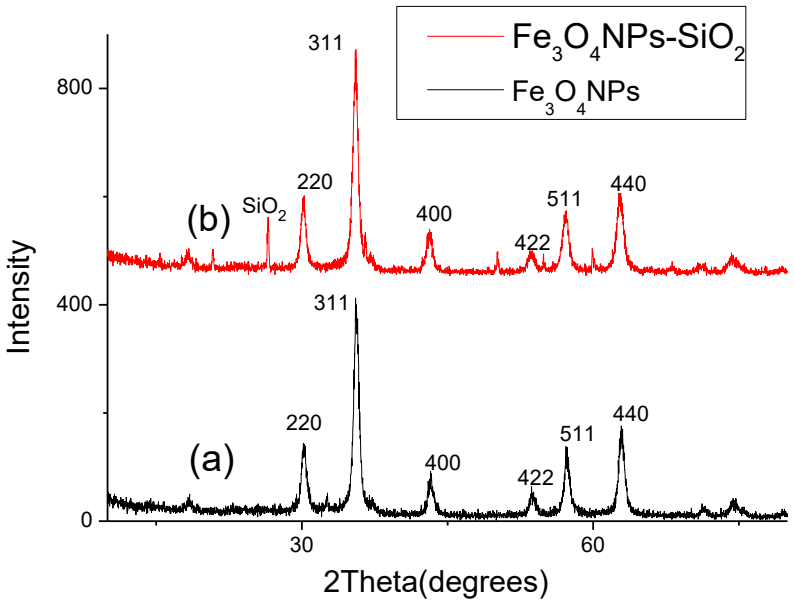


Figure 4.2 (a) XRD Spectra of Unsupported Fe_3O_4 NPs, (b) SiO2 Supported (Fe_3O_4 NPs-SiO_2)

The XRD pattern for Fe_3O_4 NPs-SiO_2 (Figure 4.2b) in addition to the above, also shows the well-defined peaks for SiO_2. The SiO_2 is of the crystalline form as the broad peak at the 2θ value of 22 degrees, a characteristic of silica in amorphous form is absent. The sharp XRD peaks at 2θ values of 20.81, 26.49 and 50.1 (overlapped by the contribution from Fe_3O_4 NPs) indicates silica in crystalline form (Saceda *et al*., 2011). Other extra minor peaks seen are expected from mixed crystalline forms present in SiO_2 and were not further elucidated.

The crystal sizes of the Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 adsorbents were determined using The Debye-Scherer′s equation (Ermias, 2015).

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad \text{.....(4.1)}$$

Where D is the average crystalline diameter 0.94 is the Scherer's constant, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity and θ is the Bragg's angle in degree.

According to the Scherrer's equation, the average crystallite size of the products were calculated for both unsuported and supported MNPs respectively and were found to be 13.5 and 12.8nm respectively.

The lattice parameter "a" and interplanar spacing d_{hkl} are determined by Eq. (4.2) Bragg's law Eq. (4.3). The values obtained areshown in Table 4.1:

$$D_{hkl} = \frac{\lambda}{2sin\theta} \quad \text{.....(4.2)}$$

$$D_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \quad \text{..... (4.3)}$$

Table 4.1 Interplanar Spacing, Lattice Parameter, XRD of Fe_3O_4NPs and Fe_3O_4NPs –SiO_2

Samples	Interplanar Spacing D_{hkl} (Å)	Lattice parameter"a_o"(Å)	Crystallite Size Estimated from XRD (nm)
Unsuported Fe_3O_4	2.51774	8.3504	13.5
Suported Fe_3O_4	2.52463	8.373	12.8

The lattice parameter and interplanar spacing for the Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 adsorbents are lower than the values reported for bulk magnetite JCPDS Card No. (79-0417) (a = 8.394 and d_{311}= 2.531) (Ghandoor *et al*., 2012), but these values are closer to the values in some references as in (Kumar *et al*., 2008). The values which are obtained for the adsorbent samples can be attributed to simultaneous formation of another phase such as γ-Fe_2O_3 (a = 8.347 and d_{311} = 2.517) (Cornell and Schwertmann 2003). The estimated crystall size of silica supported MNPs was smaller than that of unsupported MNPs which is indicative that the addition of supporting materials controls the size of the MNPs.

4.3 Adsorbent Characteristics Obtained by FT-IR Analysis

FTIR spectrum of the synthesized Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 are shown in Fig.4.3 a and b. Astrong adsorption band around 522–633cm^{-1} wavelength shows the presence of Fe_3O_4 NPs in both SiO_2 supported and the unsupported samples(Figure 4.3). This band is interpreted to the stretching vibrations of Fe^{2+} and Fe^{3+} ions in tetrahedral regions and Fe^{3+} ions in octahedral regions of magnetite (Farimani, *et al*., 2013). In the IR spectrum of Fe_3O_4 NPs (Figure 4.3 a), there are two characteristic vibrations due to the presence of Fe_3O_4 (Fe–O from isolated tetrahedral Fe_3O_4 at 642cm^{-1} and from the condensed octahedral Fe_3O_6 at 587 cm^{-1} (Jitianu, *et al*., 2006). A third expected vibration, however, from condensed octahedral Fe_2O_6 at 390cm^{-1}) 1 (Jitianu, *et al*., 2006) could not be identified due to the scanning range limitation of the instrument. The band at 1119 cm^{-1} is attributed to the Fe-OH bond due to octahedral sites of the magnetite. The broad peak at 1621cm^{-1} is attributed to H-O-H bending of water vapor adsorbed on the magnetite surface (Li, *et al*., 2012). Similarly many O-H vibrations occur

from 3160-3430 cm^{-1} due to O–H stretching mode of vibration of free water molecules and surface hydroxyl groups or adsorbed water on the NPs surface (Haw, *et al*., 2011). A sharp peak at 2360 cm^{-1} is the CO_2 vibration (Banerjee and Chen 2007).

The FTIR spectra of the Fe_3O_4 NPs-SiO_2 (Figure 4.3b) is not much different from that of the spectrum for the Fe_3O_4 NPs. The absorption bands between 800 and 1260 cm^{-1} have been described as a superimposition of various SiO_2 peaks, Si–OH.

Water shows an intense characteristic absorption band between 3300 cm^{-1} and 3500 cm^{-1} assigned to O–H stretching. Also this band can be cross checked through the 1622 cm^{-1} band due to scissor bending vibration of molecular water.

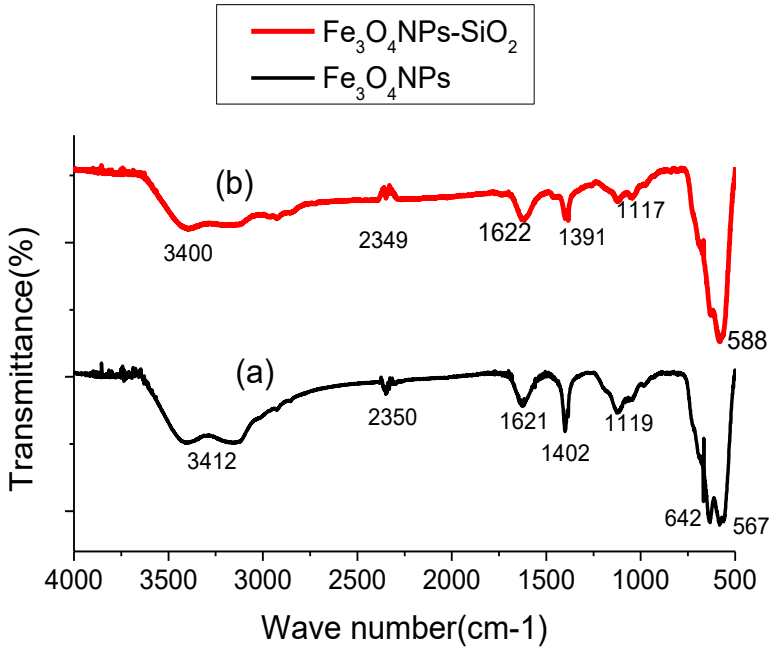
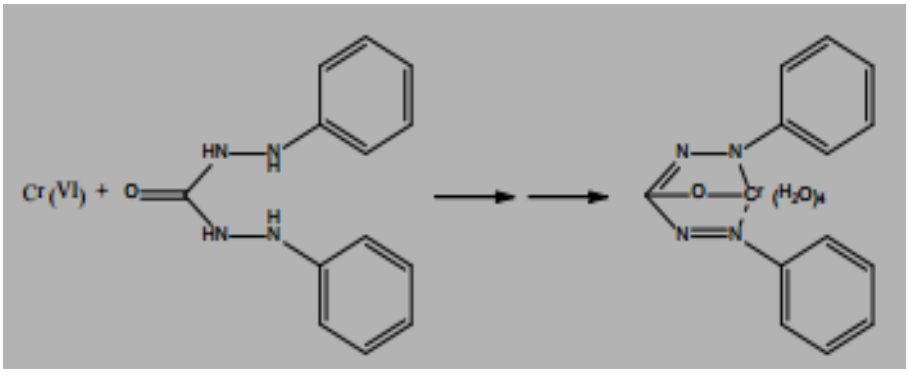


Figure 4.3 (a) FT-IR spectra of Unsupported Fe_3O_4NPs, (b) SiO_2 supported (Fe_3O_4NPs-SiO_2)

4.4 Chromium Removal Analysis

For determination of residual concentration of chromium, UV-Visible Analysis of Samples at wavelength 540nm assisted with diphenylcarbohydrazide were done. Hexavalent chromium

reacts with 1, 5-diphenylcarbazide to produce a reddish purple color in acidic solution and quantified by measuring its absorbance at its wavelength of maximum absorption.



1,5-diphenylcarbazide Cr-diphenylcarbazone complex

Figure 4.4 Reaction of Hexavalent Chromium with 1,5-Diphenylcarbazide (Tayone 2015)

A calibration equation (y = 0.0326x + 0.3392, R^2= 0.9953, where y is absorbance and x is concentration in ppm) for the quantitation of Cr(VI) in aquoes solution as indicated in the (Fig.4.5). A droplet of diphenyl carbazide solution was added into the sample (coloring purpose) before it measured. The diphenylcarbazide solution was prepared by mixing 0.25 mg of diphenylcarbazide powder mixed with 50 ml of acetone. Each sample of solutions (15ml) containing various concentrations of Cr(VI) 20, 40, 60 and 80 mg/L added into 25 ml standard flasks. To this 2 ml of 3M H_2SO_4 was added followed by 1ml of 1-5 diphenylcarbazide and total volume was made up to 25 ml using distilled water. Cr(VI) concentrations estimated by the intensity of the brownish-red color complex formed, was measured using UV-spectrometer at 540 nm. To assure data quality all the batch experimental points was duplicated.

To estimate the percentage removal of Cr(VI) from aqueous solution, the following equation was used.

$$\text{Percentage of removal Cr(VI)} = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{.....(4.4)}$$

Where, C_0 and C_e are the concentrations of Cr(VI) at the beginning and at the end of the adsorption process. The metal uptake Q_e(mg/g) at equilibrium time was calculated from the following equation.

$$Q_e = \frac{C_o - C_e}{m} \times V \quad \text{.....(4.5)}$$

Where Q_e (mg/g) is the amount of chromium adsorbed per unit weight of adsorbent, V is the volume of aqueous solution (m_l), and m is the adsorbent weight (g).

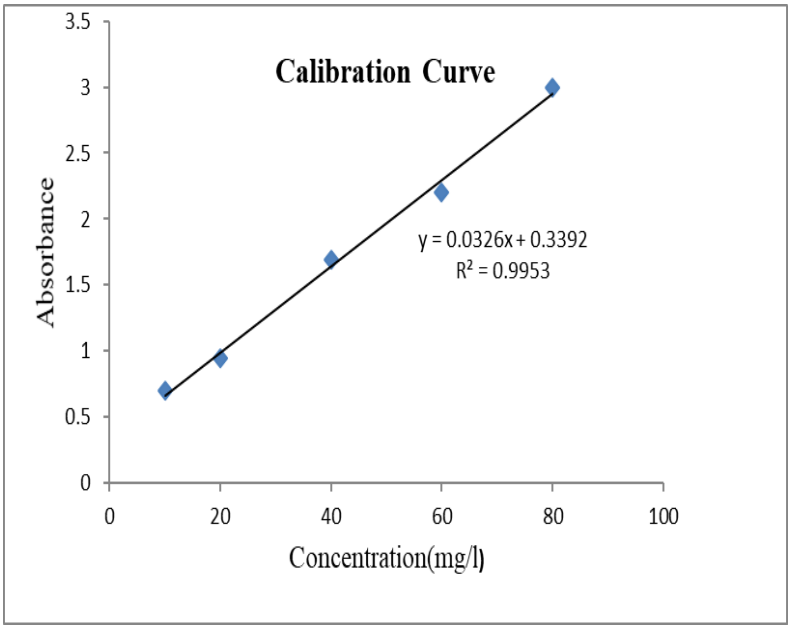


Figure 4.5 Calibration Curve for Cr(VI) Concentration Versus Absorbance

4.5 Optimization of Factors Affecting Chromium Adsorption

4.5.1 Effect of pH on the Adsorption of Chromium ions

The aqueous pH significantly modifies heavy metals adsorption, influencing surface chemistry (Chowdhury *et al*., 2012), determining the adsorbent surface charge and the degree of ionization and speciation of the adsorbed species (Ahmed *et al*., 2013). In aqueous systems, the surface of iron oxides is covered with FeOH groups (Ahmed, *et al*., 2013). Surface hydroxyl groups protonate or deprotonate to generate surface charge $FeOH_2^+$ or FeO^- functions at pH values below or above the pH_{ZPC}, respectively (Chowdhury *et al*., 2012). Its reported hydrolysis products $FeOH^+$ $Fe(OH)_2^0$, and $Fe(OH)_3^-$ vary with the pH (Cornell and Schwertmann 2003). Thus, electrostatic forces between metal ion species and surface charges are responsible for adsorption (Ahmed 2013). Magnetite′s zero point charge is the pH value at which the surface concentrations of $FeOH_2^+$ and FeO groups are equal (Petrova *et al*., 2011). The measured pH_{ZPC} (7.4) of magnetite surface is close to neutral.

Figure 4.6 shows the effect of pH on Cr adsorption by the Fe_3O_4 NPs-SiO_2 adsorbent at A dose of 0.7g and 120 minutes contact time. Maximum chromium removal of 96.5%, 88% and 80% at pH 3 for Cr(VI) initial concentrations of 20, 40 and 60 mg/L respectively. The removal increased with an initial increase in pH between 2-3 from 57.7 - 96.5%, then decreased rapidly to 50.5 % as the pH was raised from 3 to 7 and then tapered sharply to 45% with a further increase in pH 7-9. High Cr(VI) adsorption occurs in the lower pH acidic range where magnetite's surface has a net positive charge from Fe-OH_2^+ surface groups. Similar results were reported earlier (Singh *et al*., 2014). At low pH, different Cr anionic species ($Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$) coexist in water (Yuan *et al*., 2009). At pH 2–3, $HCrO_4^-$ is favorably adsorbed due to its low adsorption free energy (−2.5 to−0.6Kkcal/mol) (Chowdhury *et al*., 2012).

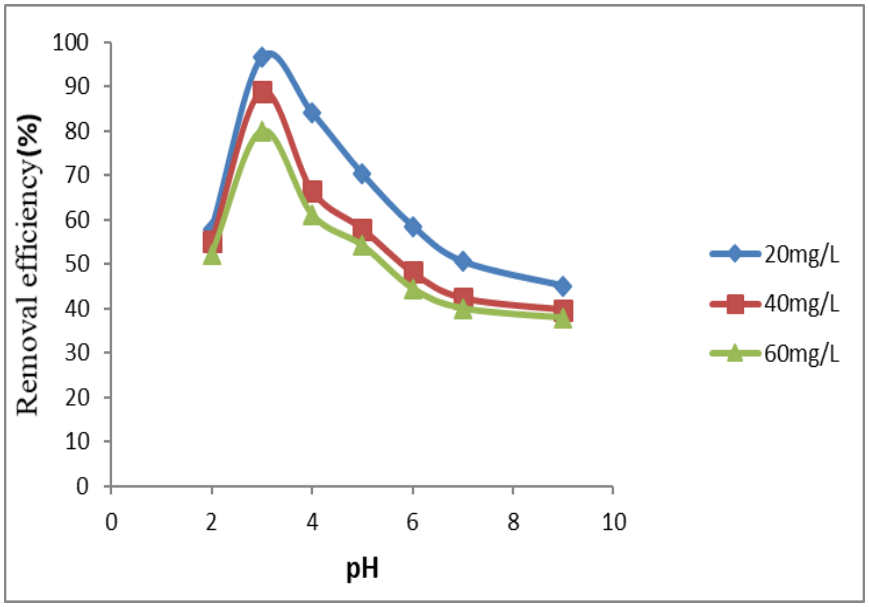


Figure 4.6 Effects of pH on Cr(VI) Removal Efficiency by Fe_3O_4NPs-SiO_2 at dose of 0.7g and 120 min.

4.5.2 Effect of Initial Chromium Concentration on Adsorption

Chromium solutions with several initial concentrations of 20, 40, 60 and 80 mg/L at room temperature and optimal pH 3 were equilibrated using 0.7g Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 adsorbent dose. Figure 4.7 shows that the Cr(VI) ion removal efficiency by the Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 adsorbents decreases from 74 to 39% and 97.4 to 55 % respectively when its

initial concentration increases from 20 to 80 mg/L. At higher initial concentrations, the active sites of the prepared adsorbents would be surrounded with more Cr(VI) ions in the solutions. In addition, the removal percentage decreases by an increase in metal initial concentration. At low initial concentrations, the ratio of initial number of chromium ions to the accessible active sites of adsorbent is low; therefore, the removal efficiency of Cr(VI) is higher and at higher concentrations, further residual Cr(VI) ions remain in the aqueous solution(Radnia *et al.*, 2012). The higher removal efficiency by the Fe_3O_4 NPs-SiO_2 adsorbent in comparison to Fe_3O_4 NPs is attributed to the presence of silica gel activated by the initial acid treatment. In the adsorption process, it is very important to consider the factors which influence the capacity of the silicas for the removal of Cr(VI) from wastewater. Amongst important factors is the structural texture and characteristics of the silica materials such as surface area, porosity, and the availability of surface silanols. For example, it has been reported that silica gels because of having high surface area, high mass exchange characteristics, and availability of high siliceous surfaces, are the mostly utilized substrate to be modified for the removal of toxic metal ions (Jal *et al.*, 2004). Another contributing factor is the smaller size of the Fe_3O_4 NPs in the Fe_3O_4 NPs-SiO_2 adsorbent as deduced by XRD analysis resulting in larger surface area and binding sites available for adsorption.

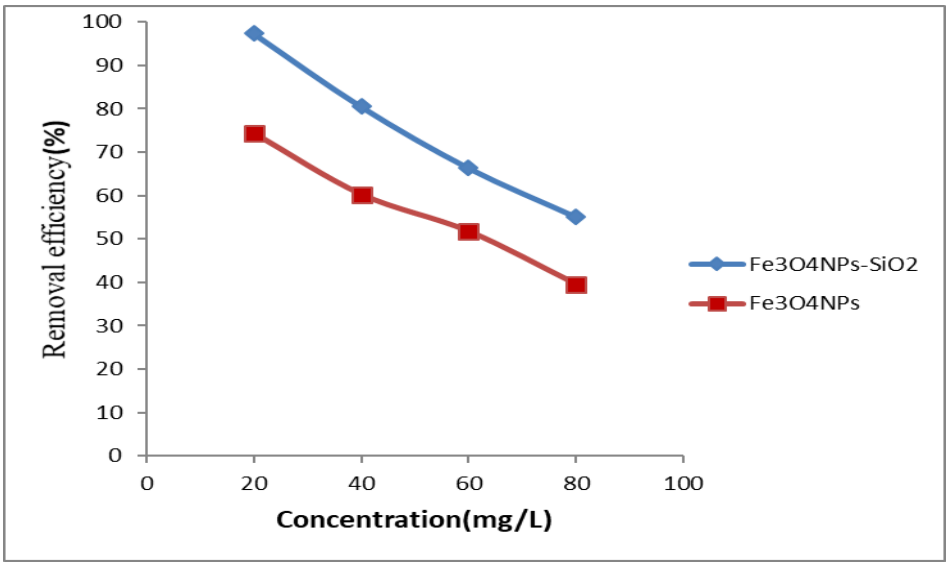


Figure 4.7 Effect of Initial Concentration on the Removal Cr(VI) by by Fe_3O_4 NPs and Fe_3O_4 NPs-SiO_2 adsorbent pH 3, Adsorbent Dose 0.7g and 120min at Room Temperature

4.5.3 Effect of Adsorbent Dose on the Chromium Cr(VI) Removal

The effect of Fe_3O_4 NPs-SiO_2 adsorbent dose in a range of 0.1g to 0.8 g on the removal of Cr(VI) ions from chromium solution concentrations of 20 and 40 mg/L, pH = 3 and 120 minutes contact time are shown in Figure 4.8. The obtained results showed that the percentage removal of Cr(VI) increased from 58 to 96.4 % and from 52 to 85% for the chromium solution concentrations of 20 and and 40 mg/L respectively with increasing amount of adsorbent dose till 0.7 g. This is explained by the increase of effective surface area on which metal ions will be adsorbed with dose. On the other hand, this would result in a continual decrease of the adsorption capacity with increase of adsorbent dose and this situation is a result of remaining of effective surface area without saturation along with the adsorption process. Similar results have been observed in the other seminal studies using different adsorbents for the removal of Cr(VI) (Li *et al*., 2008).

At an adsorbent dose of 0.8 g, the percentage removal are 95 and 84.5% for the chromium solution concentrations of 20 and 40 mg/L respectively and are marginally lower by ~1.5 and 0.5% compared to the percentage removal at 0.7g adsorbent dose. Thus, when viewed economically, 0.7g is the optimum adsorbent dose for maximum Cr(VI). Further, it is observed that under the experimental conditions, the removal efficiency of Cr(VI) modestly decreased as a function of the increase in initial concentrations of Cr(VI).

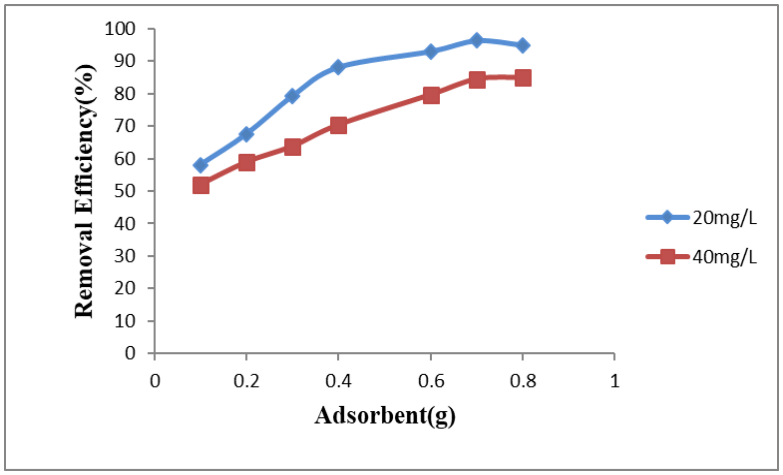


Figure 4.8 Effects of Adsorbent Dosage on Cr(VI) Removal by Fe_3O_4 NPs-SiO_2 at Concentration 20mg/L, PH = 3 and 120min, at Room Temperature

4.5.4 Effect of Contact Time on the Adsorption of Chromium Cr(VI)

The adsorption experiments were carried out for different contact times with fixed adsorbent dose, pH, and initial concentration. The results were plotted on Figure 4.9, as it is shown, the removal efficiency of chromium by the adsorbent significantly increase with contact time until a state of equilibrium is attained. During the initial stage of adsorption, high removal may be attributed to the presence of a large number of available binding sites. As the time increases, most of the binding sites get occupied with adsorbate species, resulting in the decrease of the rate of removal.

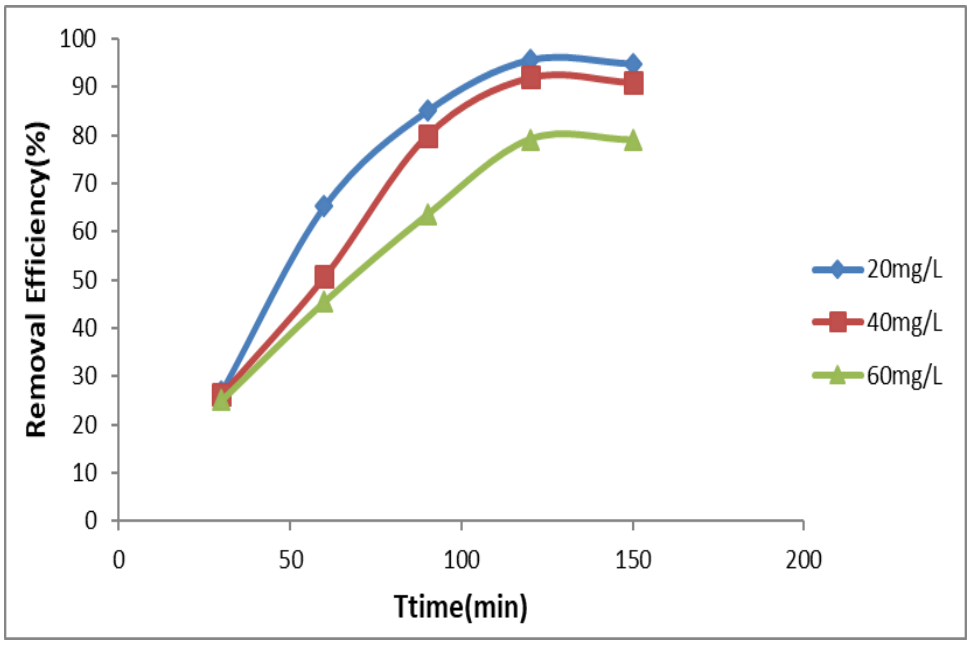


Figure 4.9 Effect of Contact Time on Chromium Removal by Fe_3O_4NPs-SiO_2 at Initail Concetration of 20mg/L, pH = 3, Adsorbent dose 0.7g. at Room Temperature

4.6 Adsorption Isotherm and Kinetics

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Adsorption isotherm models can be applied to a wide range of adsorbate concentrations in order to provide pertinent and important information for design and scale-up.

These isotherms are critical for optimization of the adsorption mechanism and the loading capacity of the adsorbent.

Freundlich and Langmuir are extensively used classical adsorption isothermal models that offer an understanding of how equilibrium is established between the adsorbate and adsorbent.

4.6.1 Langmuir Isotherm

The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface. Once a site is filled, no further adsorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved.

The isotherm is represented by

$$\frac{C_e}{q_e} = \frac{K_L C_e}{Q_m} + \frac{1}{Q_m} \quad \text{..... (4.6)}$$

C_e (mg/L) is the concentration of adsorbate left in solution at equilibrium, K_L is the Langmuir bonding energy, Q_m(mg/g) is the adsorption maximum (mg/g) and q_e(mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent.

The Langmuir constants Q_m and K_L were determined from the intercept and slope of the linear plot of (C_e/q_e) against the equilibrium concentration (C_e).

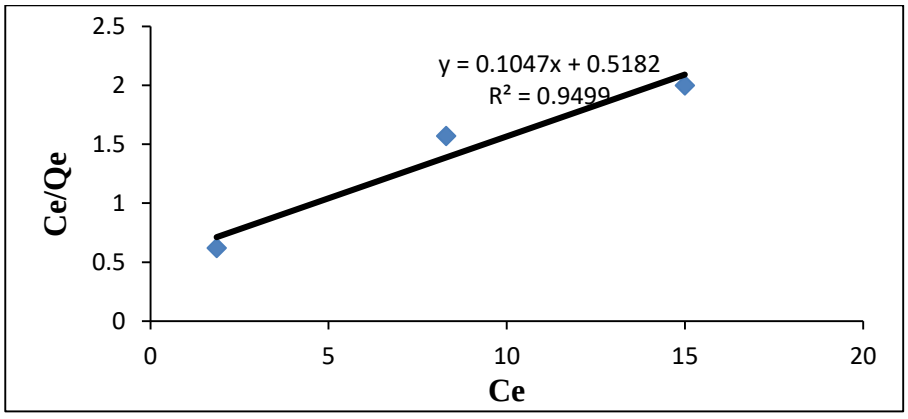


Figure 4.10 Langmuir Isotherm for Cr(VI) Ion Adsorption

4.6.2 Freundlich Isotherm

The Freundlich isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of the adsorbent.

This model assumes that

- Several layers of adsorbate can be attached on the adsorbent and adsorbate will continuously keep binding to the adsorbent and
- The energy required for adsorption is not constant, but it varies and exponentially distributed. This model can be represented by below equation.

$$\ln q_e = \ln k_f + \frac{1}{n} (\ln c_e) \quad \text{.....(4.7)}$$

Where qe is the amount of adsorbate at equilibrium time in mg/g, C_e is the equilibrium concentration of adsorbate in the solution in mg/L, K_f is the capacity of the adsorbent in mg/g and ***n*** is the adsorption constant for Freundlich in L/mg, usually greater than one. To determine the constants K_f and ***n***, the linear form of the equation may be used to produce a graph of $\ln(q_e)$ against $\ln(C_e)$(Fig. 4.11).

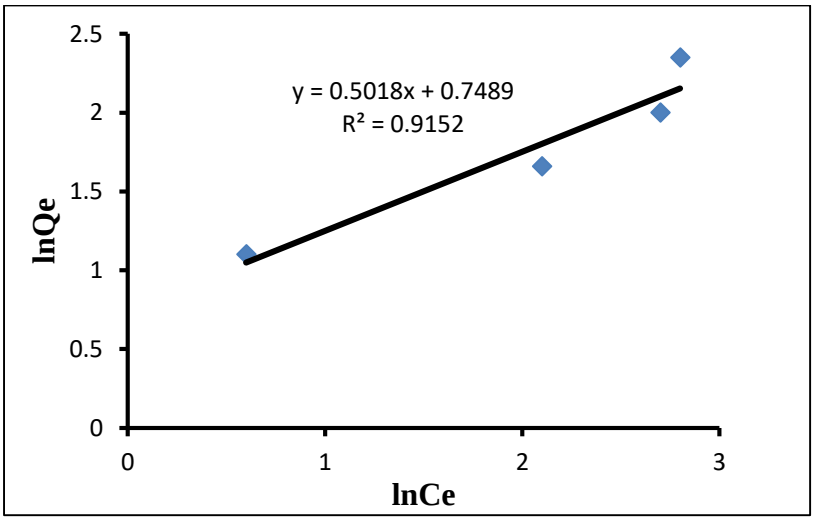


Figure 4.11 Freundlich Isotherm Model for Cr(IV) Adsorption

If n =1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one

indicates cooperative adsorption. K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models. From the above equation the value of 1/n=0.5018 while n=1.99 indicating that the sorption of Cr(VI) unto the magnetic sorbent is favorable and the R^2 value is 0.9152. The following table 4.2 shows Langmuir and Freundlich isotherm model constants and correlation coefficients for adsorption of chromium.

Table 4.2 Langmuir and Freundlich Isotherm Model Constants

Isotherm	R^2	Estimated isotherm parameters
Langmuir	0.9499	Q_m(mg/g)=1.93 K_L(L/mg)=0.20
Ferundlich	0.9152	K_f =2.11 n =1.335

The regression coefficients (R^2) for Langmuir and Freundlich isotherms are found to be 0.9499 and 0.9152 respectively. The Langmuir adsorption isotherm is the best model for Cr (VI) adsorption on to the magnetic sorbent. This may be due to homogeneous distribution of active sites onto magnetic sorbent surface, since the Langmuir equation assumes that the surface is homogenous flat surface of an adsorbent. The agreement of the Langmuir model with the experimental results suggests that a monolayer coverage of Cr(VI) on the outer surface of adsorbent Fe_3O_4.

4.7 Adsorption Kinetics

Equilibrium study is vital in determining the efficancy of adsorption. It is also necessary to identify the adsorption mechanism for a given system. Kinetic models have been exploited to test the experimental data and to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction. In addition, information on the kinetics of metal uptake is required to select the optimum conditions for full scale batch or continuous metal removal processes. Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface. Several

kinetic models are used to explain the mechanism of adsorption processes. These models include Pseudo-first-order rate model and Pseudo-second order rate model.

In order to define the adsorption kinetics of heavy metal ions, the kinetics parameters for the adsorption process were studied for contact times ranging from 0 to 2h by monitoring the removal percentage of the Cr (VI).

4.7.1 Pseudo First Order Model

The Pseudo first order rate model based on adsorption capacity of adsorbent and is generally expressed as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad \text{.....(4.7)}$$

Where, Q_e and Q_t are the amounts (mg/g) of Cr (VI) adsorbed at equilibrium and at time (t), respectively. Plot of $\ln(Q_e - Q_t)$ versus t gives a straight line for first order adsorption kinetics which allows computation of the rate constant k_1.

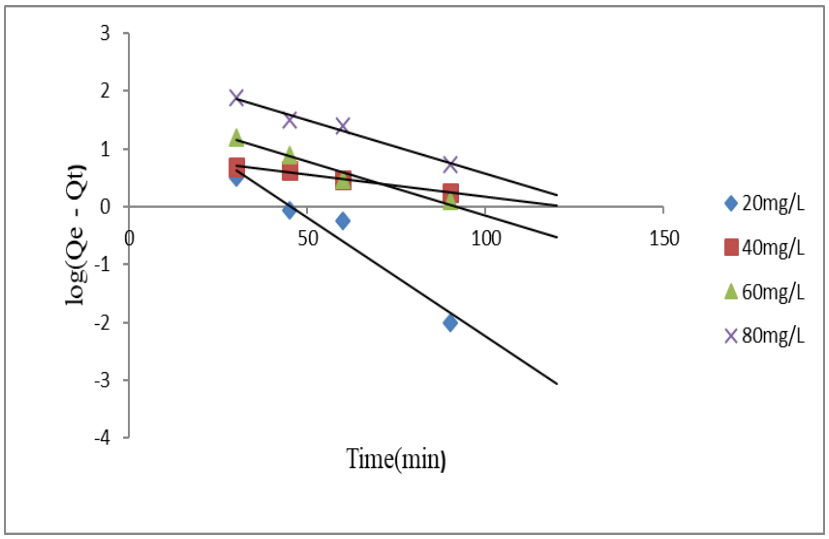


Figure 4.12 Pseudo First Order Kinetics Model

4.7.2 Pseudo-Second Order Model

The equation that describes the pseudo-second order model is given in the following linear form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1t}{q_e} \quad \text{.....(4.8)}$$

Where k_2 is the adsorption rate constant (g/mg-min), The K_2 and q_e are found from the intercept and slop of t/q_t versus t linear plot such that q_e=1/slope and k_2= slope^2/intercept.

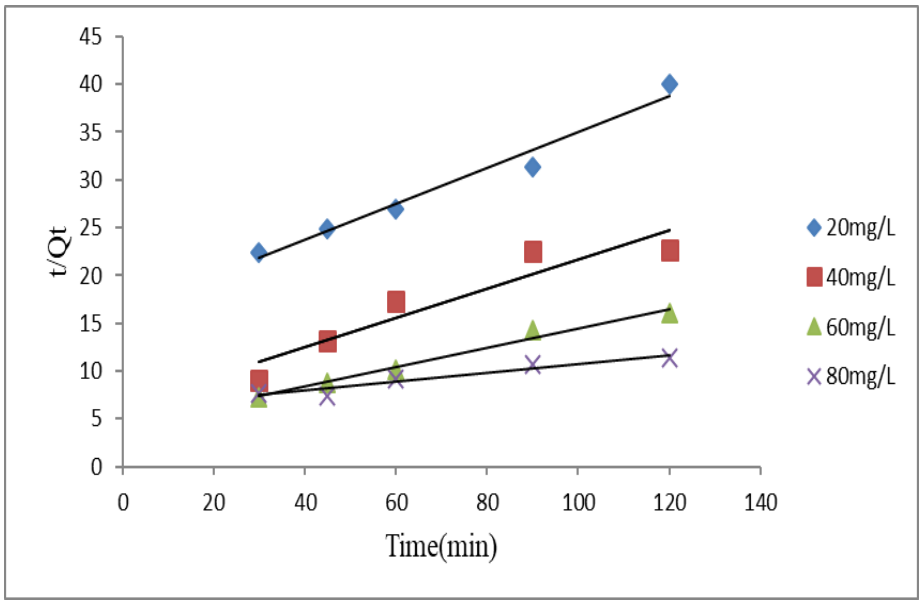


Figure 4.13 Pseudo Second Order Kinetics Model

Table 4.3 the Adsorption Kinetic Model

Initial concentration(mg/L)	Pseudo 1st order kinetic model			Pseudo 2nd order kinetic model		
	Q_e	K_1	R^2	Q_e	K_2	R^2
20	6.3	0.0411	0.9503	5.3	0.0117	0.9724
40	2.5	0.0075	0.9787	6.5	0.024	0.884
60	5.5	0.0187	0.967	9.87	0.023	0.9839
80	11.2	0.0186	0.9781	21.5	0.00768	0.9252

To identify the ratecontrolling mechanisms during the adsorption of Cr(VI), two simplified models were applied to evaluate the experimental data. The goodness of the fit was estimated in terms of the coefficient of determination, R^2. In this work, the pseudo-first-order and pseudo-second order kinetic models were selected to test the adsorption kinetics.

The degree of goodness of linear plot of these kinetic models can be judged from the value of the determination coefficient of the plot, which can also be regarded as a criterion in the determination of the adequacy of kinetic model.

From the above table Pseudo First-order which considers physisorption as the rate limiting step present high correlation coefficients than pseudo-second order kinetics and the experimental q_e values obtained are closer to those calculated for the first order model.

4.8 Desorption Studies

After adsorption experiments, the MNPs with the adsorbed Cr(VI) ion were separated by filtering from the solution and then added to various stripping solutions and agitated at 100rpm for 90min and the final Cr(VI) concentration was determined. Desorption of metal ions from adsorbent was carried out using dilute NaOH, KOH, HNO_3 and HCl solutions. Table 4.4 shows the desorption of chromium (VI) from the magnetic sorbent with various desorption agent.Effective desorption was obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. The desorption efficiency (DE) was determined using the following Equation.

$$DE = \frac{C \times V}{q \times m} \times 100 \quad \text{.....(4.9)}$$

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

Table 4.4 Desorption of Cr(VI) from Adsorbent

Desorption agent(1M)	Desorption %
NaOH	73.6
KOH	54.8
HCl	41.25
HNO_3	33.6

Table 4.4 shows the recovery of Cr (VI) under 4 different pH of regeneration solution. It shows that at higher pH, the recovery of Cr(VI) and regeneration of adsorbent was higher. The main compound lead the Cr(VI) being recovered is OH^-. At low and neutral pH, the concentration of OH^- is lower than alkaline solutions, so the Cr(VI) recovery percentage is lower. Therefore NaOH Solution as selected as regeneration solution at desorption tests.

5 Conclusions

A successful preparation of silica supported IONPS for the removal of Cr(VI) from aqueous solutions were carried out. The nanoparticles were synthesized by the co-precipitation method. It is known that it is expensive and ineffective to remove Cr(VI) ions from aqueous solutions using conventional methods when the chromium concentration is low. An adsorption process using magnetic sorbent, is an ecofriendly and low-cost method that could replace conventional processes for remediating Cr(VI) pollution in aqueous systems. The batch technique is used to study the adsorption as a function of various influencing factors such as initial metal ion concentration, contact time, pH magnetic sorbent dosage and under ambient conditions. The obtained results indicate that the adsorption percentage increases with increasing the amount of dosage and contact time until it reaches the equilibrium values and decrease with increase in the amount of initial metal ion concentration. The percentage removal was found to be dependent on the quantity of sorbent dosage, pH, time, and initial concentration of the sorbate(chromium). The kinetic studies indicate that adsorption of Cr(VI) can be described well by pseudo-first order models. Effective desorption was obtained with alkaline solutions. This shows that at higher pH, the recovery of Cr(VI) and regeneration of adsorbent was higher.

6 Recommendation

More research is needed to study the dependence of particle size, agitation speed and temperature on the synthesis of nanoparticles. It needs the collaborative efforts of research and industrial persons to materialize a dream of fast, economical and feasible water treatment technology. Uncertainties over the health impacts and environmental fate of these NPs need to be addressed before their widespread application.

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Appendixes

Appendix 1: Raw Data for the Effects of Different Parameters on the Removal Efficiency of Cr(VI) by IONPs

Appendix 1.1: Effect of pH on the removal efficiency of Cr(VI) by IONPs

pH	**20mg/L**	**40mg/L**	**60mg/L**
2	57.75	55	52.2
3	96.5	88.9	80
4	84.09	66.5	61.125
5	70.25	57.9	54.2
6	58.5	48.1	44.5
7	50.5	42.3	40.01
8	47.75	41	38.955
9	45	39.7	37.9

Appendix 1.2: Effect of initial concentration on the removal efficiency of Cr(VI) by IONPs

Concentration(mg/L)	**Fe_3O_4-SiO_2**	**Fe_3O_4**
20	97.4	74.34
40	80.5	60.23
60	66.3	51.7
80	55	39.5

Appendix 1.3: Effect of adsorbent dose on the removal efficiency of Cr(VI)

Adsorbent(g)	**20mg/L**	**40mg/L**
0.1	58	52
0.2	67.5	58.9
0.3	79.3	63.8
0.4	88.2	70.4
0.6	93.1	79.7
0.7	96.4	84.5
0.8	95	85

Appendix 1.4: Effect of contact time on the removal efficiency of Cr(VI) by IONPs

Time(min)	**20mg/L**	**40mg/L**	**60mg/L**
30	26.75	26.2	25.1
60	65.2	50.6	45.5
90	85	80	63.5
120	95.6	92	79.125
150	94.8	91	79

Appendix 2: Parameters for plotting Langmuir and Freundlich Adsorption isotherms of Cr(IV)

C_0(mg/L)	C_e(mg/L)	1/Ce	lnC_e	Q_e	1/Qe	lnQe	Ce/Qe
20	1.86	0.537	0.62	3	0.33	1.1	0.62
40	8.3	0.12	2.1	5.28	0.189	1.66	1.57
60	15	0.067	2.7	7.47	0.134	2	2
80	16.8	0.059	2.8	10.5	0.095	2.35	1.6