Synthesis of Nickel-Ferrite Nanoparticles (NFN's) for Removal of Heavy Metals from Wastewater

Submitted by

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CERTIFICATE

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This thesis is dedicated to my Parents & Siblings

For their endless care, support, encouragement and patience

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Waheed Ali Khoso

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List of Abbreviations

AAS	Atomic Absorption Spectroscopy
Cd	Cadmium
Cr	Chromium
DPC	Diphenylcarbazide
EDS	Energy Dispersive Spectroscopy
eV	Electron volt
FWHM	Full Width of Dif. line at Half of Max. Intensity
HM	Heavy Metals
IESE	Institute of Environmental Sci & Engineering
MCL	Maximum Concentration Level
NEQS	National Environmental Quality Standards
NFN’s	Nickel Ferrite Nanoparticles
Pb	Lead
PCRWR	Pakistan Council for Research in Water Res.
RO	Reverse osmosis
SEM	Scanning Electron Microscopy
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
WHO	World Health Organization
XRD	X-Ray Diffraction

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Abstract

In the present study, efficiency of prepared nickel ferrite nanoparticles (NFN's) in synthetic wastewater for chromium, lead and cadmium removal by batch adsorption method has been investigated. Ions of heavy metals present in water poses danger to the environment and public health due to their toxic nature. In this work, magnetic nickel-ferrite nanoparticles (NFNs) ranging in size 60 – 80 nm were synthesized using the co-precipitation method at 70±5°C followed by calcination at 350-550 °C. The crystalline structured particles with ferromagnetic properties were thus obtained and thereafter characterized in order to ascertain their structure, composition and morphology. The adsorption parameters under study were pH, dose and contact time. The values for optimum removal through adsorption were investigated at various parameters (pH: 3 - 7, dosage: 10, 20, 30, 40, 50 mg and contact time: 30, 60, 90,120 minutes) by use of NFN's as adsorbent. Removal efficiencies of chromium, lead and cadmium was found up to 89%, 79% and 87% respectively under optimal operating conditions. The optimization of the parameters was studied by changing a parameter at one instant, keeping the other constant. Highest efficiency obtained for chromium lead and cadmium removal through NFN's was observed at a contact time of 90 mins, low pH (e.g. 3 to 5), adsorbent dose 30 mg per 10 mL of sample solution (e.g. 300 gL^{-1}) and average speed of shaking – 250 rpm. The experimental data revealed the parameters of adsorption which are contact time, pH and adsorbent dose and nature of metal ions are strongly influential in measuring adsorption. It was found that pH has influential and dominant relation on metal ions adoption.

CHAPTER 1

Introduction

1.1. Water Pollution

Degraded quality of water and contamination is major isuue impacting the water safety such as lakes, rivers, seas, oceans and groundwater. It happens when contaminants enter the water supply without treatment. Waste from houses, factories and other structures is dumped into water bodies and as a result, water is polluted (Wang et al., 2012). These contaminants, especially heavy metals pollution in water, is becoming a dormant problem of global environment (Tripathi et al., 2015). Untreated Household wastewater, agriculture and waste from industrial sector, like mining, electroplating, metallurgy, chemical plants, are responsible for water bodies contamination with heavy metals (Husnain ., 2015). Rapid industrialization is a major threat for causing water pollution as industrial wastewater from many industries releases heavy metal ions like leather, textile, paints and pigments, fertilizer and chemicals are released into water body. Such as chromium, mercury, lead, phosphorous, copper, cadmium and iron are extremely toxic with a high solubility in water (Tchounwou et al., 2012) and they considered as most dangerous element because they are very durable and irresolvable (Dargahi et al., 2016). Wastewater contains hazardous, toxic and non-biodegradable materials into harmless-end-products unlike organic that cause serious health threats and poses menace to the environment (ElSayed., 2018). Presence of heavy metals in wastewater are known to cause serious health issues. Since few decades, the huge amount of wastewater discharged into freshwater bodies from many sources that can pollute surface water bodies as well ground water (WWF., 2007). Removal of such ions of heavy metal specially from wastewater of industries is an area under focus by many scientist and researchers since the last few decades throughout the world to meet the local environmental standards. Industries need to treat the wastewater before it mixes with major resources of water (Krishna et al., 2012).

1.2. Problems in Pakistan

In Pakistan, about 60% of used water is discharged into streams without treatment. It has been on record that almost 15 million people are deprived of clean drinking water and almost 70 million people lacks proper sanitation system in Pakistan. (Yang et al. 2019 and Nisar 2014). As repeated by health organizations above 1.1 billion humans are affected because of poor availability of proper human use water (Kazi et al., 2019). Wastewater pollution is a major issue in most countries including Pakistan with a dense population and increasing rate of urbanization (Ali., 2017). Pollution caused by human is severely affecting modern human society and is considered to be a a major challenge (Yang et al., 2019).

1.3. Effect of Polluted Water on Health

Human health is deeply affected by heavy metals as presence of these metals leads to its biological accumulation in the upper food chain (Verma et al., 2013). Water polluted with heavy metals, pesticides, POP's and other health threatening chemicals, it increases the chances of cancer, damage of kidney, neurological, central nervous function, lung disease(Järup et al., 2003), Reproductive diseases and hormonal imbalance can be caused with the accumulation of heavy metals (Tchounwou et al., 2012 and Dargahi et al. 2016).

Heavy metals pollution poses a significant threat to our natural environment. Natural sources of heavy metals are volcanic eruptions, change in weathering metals containing rocks and anthrophonic sources such as mining, coal industries emissions, agricultural pollutants include pesticides and phosphate fertilizers etc (Khan., 2019). Due to Rapid industrialization, influent contaminates both the fresh surface and groundwater (Rai et al., 2018). These metals can easily be transported in wastewater at effluents point as well at the place where it is discharged too especially near industrial zone areas (Turdean et al., 2011). Heavy metals can affect aquatic microorganisms in water because it transfers from water into microorganisms cells where chemically change involve in slowly damaging their organs and circulate into the human body by food chain (Masindi et al., 2012 and Federico et al., 2016).

1.4. Technique for Removal of Heavy Metals

Many researchers have worked on the development of Nanoparticles that are more efficient for wastewater treatment. All possible methods are cost-effective, environment-friendly and almost zero sludge end products (Azimi et al., 2017 and Tripathi et al., 2015). Since few decades the field of nano-science has been widely emerged with rapid growing research (Sagadevan et al., 2017) Nano particles of iron ferrite has produced some promising results in different disciplines. Although recently it has been investigated in the discipline of wastewater treatment for heavy metals removal. Many forms of evidence have shown that material of nano size Can serve as physical sorbents for heavy metals removal. Nano ferrite material has also been stated finest method for wastewater treatment (Barakat et al., 2011).

1.5. Nickel Ferrite Nanoparticles and its Application

Ferrite has benefit of its properties of ferrimagnetism, stability and low conductivity because of its counter spinel structure. Ferrite nanoparticles in the nanoscience field is in which nanoparticles are prepared with special features of having wider and larger site surfaces with having smaller size mean large area: volume (Dargahi et al., 2016). These NFs form a cubic structure and each corner of a ferrite cell unit consists of a ferrite molecule. (Vinosha et al., 2017).

Currently, Research on Nickel Ferrite Nanoparticles (NFN's) has been an accepted method due to their broad application and usage in physical, chemical and magnetic properties because of their free atoms or molecules (Syam et al., 2014). Various methods have been developed for preparations of NFN's like co-precipitation method, gel hydrothermal method, thermolysis, self-propagating, but the co-precipitation method for synthesis of nickel ferrite nanoparticles is simple and inexpensive (Sagadevan et al., 2017). This method also epitomized the need of application of NF nano-particles for the sustainability of environment (Saif et al., 2016).

Many studies confirmed has reported that adsorption is best and effective method, due to cost effective in treating wastewater (Tripathi et al., 2015). It also plays an imperative function in determination of physical properties at nano scale for removal of various kinds of contamination by nanomaterials (Sagadevan et al., 2017 and Lu 2019), few studies confirmed that synthesized nanomaterials are less toxic as compared to heavy metals (Saif et al., 2016). These NFN's were used many scientists as adsorbent material in wastewater application (Sadegh et al. 2017 and Maiti et al., 2020).

1.6. Heavy metals Removal Metals through Adsorption

Heavy metals removal is of great importance from ecosystem and literature has showed that it has received attention. Up to date, various methods include ion exchange, filtration and adsortion has been explored (Barakat et al., 2011 and Wang et al., 2012). Among these techniques, one of the most common technique is adsorption, as its environmentally friendly and has minimal economic cost. The process of adsorption is a surface physical phenomenon in which the targeted substance or known as adsorbate accumulates on the surface of adsorbent (Sadegh et al., 2017 and Houari et al. 2019). HM's removal through nano particles has been extensively used because of its economic feasibility (Wang et al., 2012; Giraldo et al., 2013 and Lu et al., 2019). Usually, substance in which the liquid and solid interface carries out is known as adsorbate. The substance or particles which gathers heavy metals is known as adsorbent (Nadeem., 2016). Capacities of adsorption for removing contaminants from wastewater economically feasible and are most environmentally acceptable way used to solve several environmental problems (Wang et al., 2012 and Gisi et al. 2016). Promising results have been reported because of the outstanding properties of magnetism of ferrites in the field of adsorbents (Sagadevan et al., 2017); several pieces of research have reported that nano-sorbent are very useful for metal ions removal from wastewater.

1.7. Problem Statement

Water, the most important natural resource which is required for the development of entire living ecosystem. Higher demand of water, along with the growth of industrialization and urbanization, has contributed to a problem of scarcity of water, which has limited and can have drastic impacts on economic development. Contamination of water is one of the major challenges to public health in Pakistan, as contaminated or used water contains dangerous and non-biodegradable materials that cause serious problems due to their toxic effects on humans and the environment. (ElSayed., 2018). In various parts of Pakistan, HMs in water cause serval health problems (Khan., 2015). Therefore, it is necessary to treat wastewater according to national and international guidelines to make it fit and healthy for human use (Zekić et al. 2018 and Dargahi et al. 2016).

1.8. Scope of study

A great deal of attention has recently and wide application in wastewater (nanowire and nanoparticle) that have fascinating magnetic and electrochemical properties. Ferrite nanoparticles are currently attracting significant attention due to their magnetic properties. Among the different ferrites, nickel ferrite has desirable magnetic properties used widely with high frequencies in various field. Several studies have shown that nanoparticles, particularly metal oxide nanoparticles are best option for wastewater treatment.

1.9. Aim of the Study

This work aimed to prepare ferrite ($NiFe_2O4$) by using chemical coprecipitation technique for heavy metal ions removal from wastewater. These NFN's were used in wastewater for removal of metal ions. Experimental parameters such as contact time, dose and pH were used to investigate the adsorption efficiency of NFNs under optimal conditions.

1.10. Objectives

- Preparation and characterization of nickel-ferrite nanoparticle ($NiFe_2O_4$) by using co-precipitation method.
- To study efficiency of nickel-ferrite nanoparticles for removal of heavy metals from synthetic wastewater.

CHAPTER 2

Literature Review

2.1. Introduction of Heavy Metals

Most of metals are very durable, irresolvable and most dangerous contamination in wastewater because these have capability to accumulate human body over a long period (Dargahi et al., 2016 and Masindi et al., 2012). They are pathogenic and can cause serious problems to human and aquatic life even at low concentrations because they are toxic materials (Verma et al., 2005) to damage human organs such as kidney problems, lungs and damage nervous systems (Yang et al., 2019 and Tchounwou et al., 2012a) and is considered dangerous due to their ability of bio-accumulation in living organisms to damage human organs (Alguacil et al., 2018; Tripathi et al., 2015 and Dargahi et al. 2016) damage to reproductive systems and even cause death (Dargahi et al., 2016).

Two kinds of metals are essential and non-essentials metals and are grouped into three categories according to their toxicity.

i) The first group is considered non-essential toxic even at a low amount of concentration that includes chromium, lead, cadmium, mercury and arsenic, etc.
ii) The second group is known as non-essential less toxic heavy metals they considered toxic at very high amounts of concentration such as arsenic, indium and bismuth, etc.
iii) and the third group of heavy metals are known as essential non-toxic metals because they are necessary for different chemical and biochemicals processes in living bodies and considered as toxic only at above a certain concentration. that includes zinc, copper, iron and cobalt etc.

Non-essential toxic heavy metals having the capacity to damage all living thing include plant, animals, eco-lives and humans at a very low amount (Verma et al., 2013) but also essential non-toxic cause adverse health effect at a very high amount of concentration (Ali et al., 2019). Their toxicity depends upon some main factors such as dose, route of exposure and chemical species and some sub-factors such as age factor, gender, genetics (Tchounwou et al., 2012b) duration, rate of exposure to toxic heavy metals (Järup et al., 2003).

2.2. Concepts in Exposure Assessment

The Risk Assessment Process:

The primary concept of exposure assessment is to develop risk assessment to understand the primary route of the risk assessment process to estimate risk and this process required four steps to evaluate potential health effects of toxic materials when human exposure to it.

- **Hazard identification:** to identify adverse effects when object expose to a harmful agent
- **Dose-response assessment:** process to estimate the toxicity of an agent by evaluating quantitative value between dose and response.
- **Exposure assessment:** process to estimate the rate of exposure to the agent(s) of concern to the human receptor.
- **Risk characterization:** to estimates the adverse effects resulting from human exposure along with uncertainty in the findings.

Exposure is to interaction between a hazardous agent object or an incident that happens when there has been interaction between human to hazard material with a particular hazards for some time" could be through the airways (inhalation), the skin (dermal contact) or the mouth."(Järup et al., 2003).

2.3. Elements of Concern in this Study

2.3.1. Chromium (Cr)

Chromium is hard and silvery having atomic number 24 and placed in the 6th group of periodic tables. It is persisting in the form of different valences like Cr (III) or Cr (VI). Chromium element in human being with 50 -200 μg/L daily intake recommended to adults and the human body can detoxify the chromium (VI) into chromium (III) (Article., 2016). Whereas hexa chromium is more hazardous to the animals, plants and human being, Cr is corrosive, toxic and potential carcinogens can damage cell membranes & biological molecules (Singh et al., 2011) It should be removed from the wastewater before their release into environmental bodies (Federico et al., 2016). India, Canada give the MCL value 0.05 to 0.008 for chromium. PCRWR Pakistan, FAO and some other countries include California New Mexico gives the 0.10 mg/l for chromium while EU gives 0.05 mg/l for irrigation use (WWF., 2007).

2.3.2. Cadmium

Cd is also known as hazardous and most toxic material by nature it is a very soft and silvery-white color having atomic number 48. It is a member of 12 groups and having specific gravity 8.6 times more than the water. Due to toxicity by nature, if consumed even a small amount over a long time it can damage the kidney, liver and bones become weaker depending upon the severity of exposure (Singh et al., 2011). Cadmium is also present in our natural environment (Air, Water, Soiland even in non-polluted seawater. It is emitted in natural air from industries and mines that using the cadmium compound like alloys, plastic, batteries, etc that source controls at an emission place up to MCL limit to prevent the quality of natural environment (Morais et al., 2012). India and Canada propose 0.01 – 0.005 mg/L. while the EU, California, Pakistan (PCRWR) set the value approximately 0.01 mg/Land NEQ's gives less than 0.1 mg/L. FAO recommended MCL of cadmium about 0.01 mg/L (WWF., 2007).

2.3.3. Lead (Pb)

Lead is a silvery, soft and denser heavy metal than another common element having atomic number 82 more heavy than chromium and cadmium and can found in group 14 of periodic tables. The main source of lead where it comes are landfills, combustion of fuels, pesticides and fertilizer base industries and exhausted gases from vehicles. It can be found in the form of sulfides and carbonates. It is the leading environmental pollutant and endangering the living world. Lead can be absorbed very rapidly into the bloodstream and red blood cells in the form of Pb^{2+} and 90% is deposited in the bones in the form of $Pb^3(PO_4)^2$ (Federico et al., 2016). Lead has no essential function in humans (IPCS., 2001 and Morais et al., 2012) and can damage the most organs of human body (Singh et al., 2011). India and Canada give MCL values for lead are to 0.1 mg/l. Pakistan (PCRWR and NEQS), FAO and California and EU set the MCL 0.50, 0.2, 0.5 and 0,05 mg/l where FAO gives 5.0 mg/l for plant growth (WWF., 2007).

2.4. Effect of Heavy Metals (HM's) on Environment & Ecosystem

HM's are considered as hazardous can accumulation in environment to cause adverse effect (Yang et al., 2019). They can found in soil, water rocks etc as natural sources to release Hm's that pollute and affects the natural environment through metal corrosion, atmospheric deposition and soil erosion (Tchounwou et al., 2012a), while they can found in mining, agriculture and industry sectors are the main anthropogenic sources of HM's (Ali et al., 2019 and Masindi et al., 2012).

HM's uptakes by plants and can easily accumulate in any living species when plants consume by human and it transfer from specie to specie with an increase in concentration through food chain called 'biomagnifications' (Singh et al., 2011) causes serious threaten for both flora and fauna at high concentrations and toxicity process of metal ions depend on pH (Husnain., 2015). Heavy metal concentration limits are not toxic for plants under range (Barakat et al., 2011; NEQS 2019; Article.,1996 and US EPA 2016). All Metals are non-biodegradable and produce toxic effects in plants and animals (Federico et al. 2016 and Verma et al., 2005).

2.5. Effect of Heavy Metals of Human Health

HM’s are poorly absorbed by the human body through any route by direct ingestion, inhalation through mouth or nose, dermal contact through skin and the parenteral route to some extent (Tchounwou et al., 2012a and Ali et al., 2019) to effect human organ problems include skin cancer, lung, gastrointestinal tract (Husnain et al., 2015) and may cause kidney damage (Järup et al., 2003), lungs disease, neurologic or psychological disorder, hearing loss, hematologic and immunologic disorders (Tchounwou et al., 2012a) dermatitis and organ damages and respiratory problems, nervous disorders & digestive system problems, damage to reproductive, renal tubular damage especially weakness of bones and many other types of cancer (Dargahi et al. 2016 and Järup et al., 2003). When Skin contact with heavy metals can cause skin allergies, dermal necrosis and dermal corrosion (U.S.EPA., 2019). The people who smoke cigarettes are more vulnerable to heavy metals (WHO., 1996). Plants intake HM’s and these plants consumed by humans ultimately circulate in food chain (Ali et al., 2019) and non-biodegradable nature human body cannot metabolize it and remain in human body over long period (Singh et al., 2011).

Humans are omnivorous and omnivorous are person or animal that eats both plant and animals. In daily life human beings are exposed to toxic Hm’s through many food items with eating meat, fish and vegetables, etc all that poses a threat to human health, some researchers reported that biomagnification of Hm’s in only a few food chains. In biomagnification cases of Hm’s in food chains, species at high risk at the higher trophic level in the food chain it means species is at greater risk level (Ali et al., 2019).

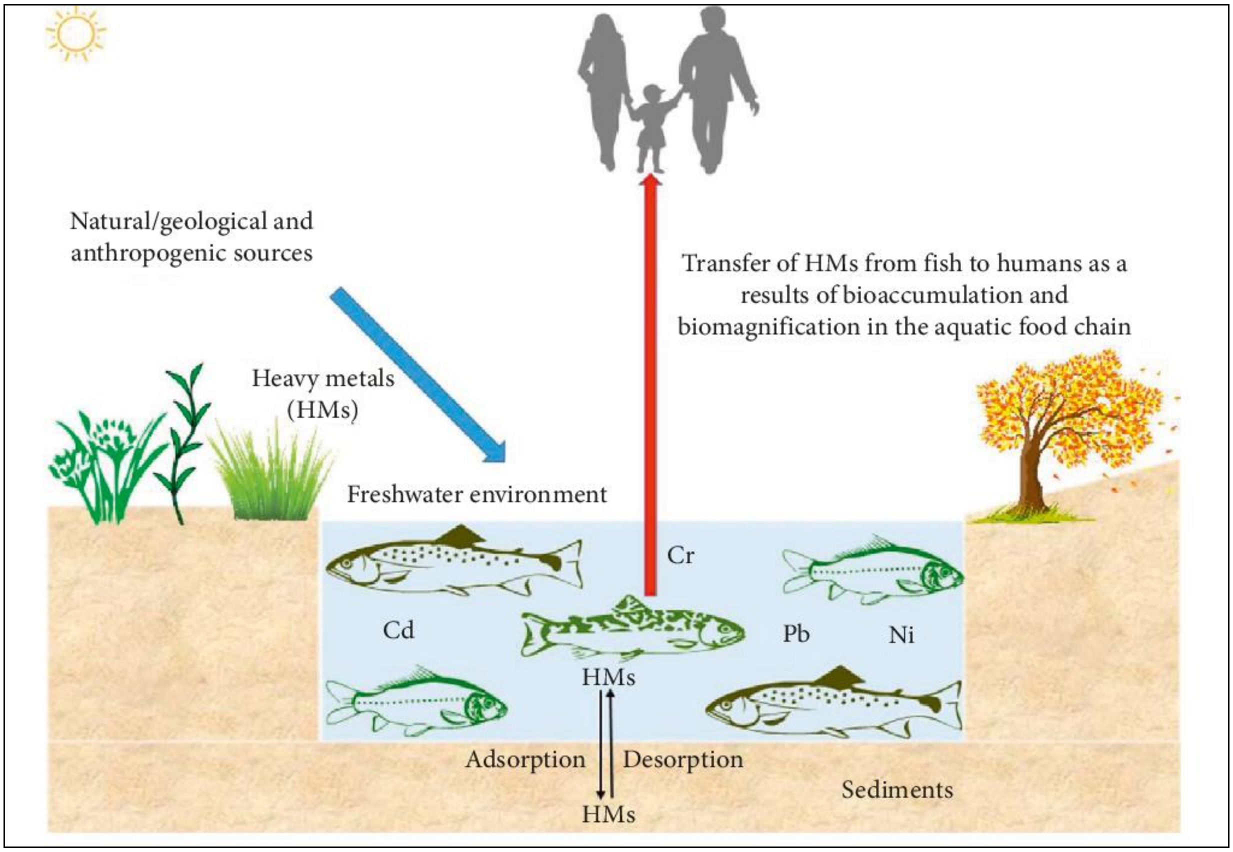


Figure 2.1: Transfer and Transport of Contaminants Through Food Chain (Hazrat Ali et al., 2019)

2.6. Effect of Heavy Metals on Animals and Plants

HM's cause hazardous due to their nature to accumulate in both plants and animals over a long period at biomagnification conditions in water and food where the concentration of Hm's increases from one specie to another specie was each level consumes another in the ecosystem (Federico et al., 2016). All living species include micro-species, plants and animals are dependent on water, food and air for their survival and they all segment are containing contaminations at high concentration include Hm's, they transfer into species or maybe transported inside the cells (Turdean et al., 2011). Toxic metals uptake by animals and plants can causing serious problems to both fauna & flora. Pollutants in the aquatic system that can damage the whole eco-life includes micro-species, fishes, the growth of plants such as germination process, aquatic ecosystem (Singh et al., 2011) and damages even physiological processes such as photosynthesis, water relations and mineral nutrition supplies and also it has been reported by many researchers that “as pH of water decreases, increase toxicity to affects earthworm life cycle" (Husnain., 2015). Many species require a small amount of some essential HM’s, such as Zn, Cu, Mn, Co and Fe which affect the water surface system (Turdean et al., 2011) at even a small amount of dose, influence both the plant and aquatic life (Ali et al., 2015) can transfer in the food chain from one trophic level to another as shown in the below figure and pollutant may extent of accumulation in plants and animals in an ecosystem depends upon their rates of elimination and rates of accumulation. therefore different HM’s may different half-lives for different species (Ali et al., 2019).

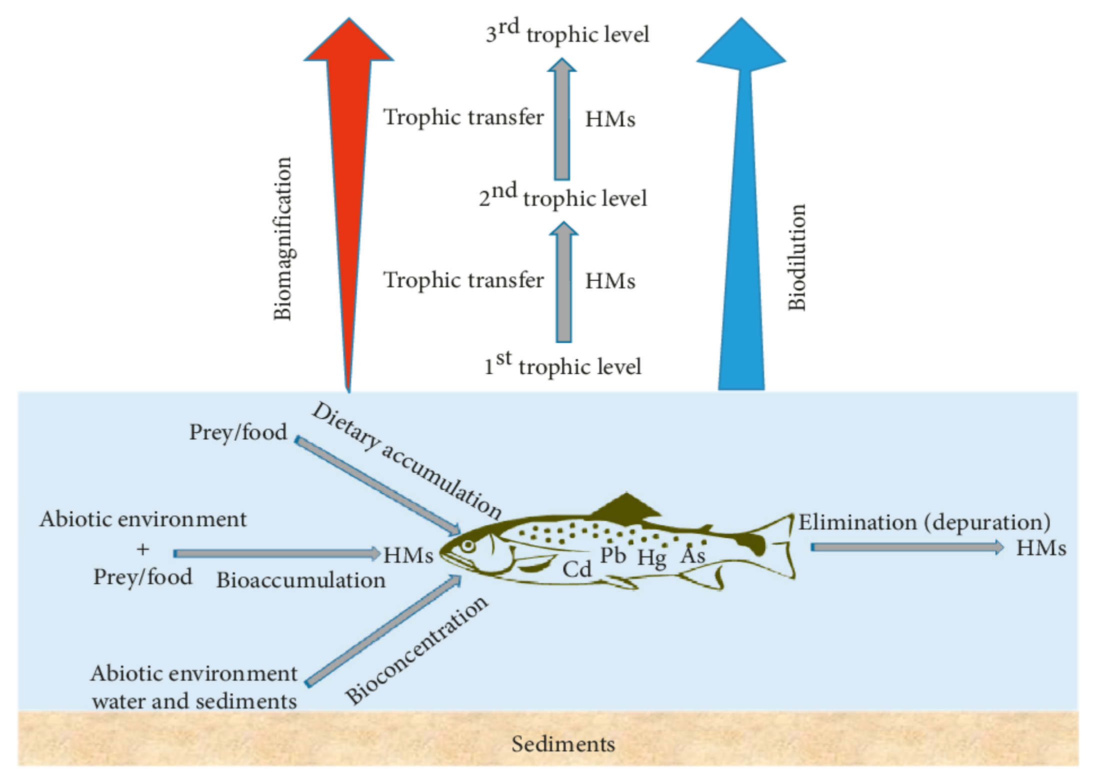


Figure 2.2: Quantification of Trophic Transfer of Heavy Metals in Ecosystem (Ali et al., 2019)

2.7. Heavy Metal Removal Methods

Various methods are classified into chemical treatment, physiochemical treatment, adsorption and advance or current treatment (Azimi et al., 2017) that includes coagulation and flocculation, chemicals precipitation, ionic change, activated carbon, carbon nanotubes, nanotechnology, electro-flotation, electrodeposition, photocatalysis, RO and membrane filtration processes (Khan., 2015; Wang et al., 2012; Barakat et al., 2011; Nisar., 2014 and Noor et al., 2014). All above methods have their advantages as well as limitations in industrial applications are outlined. Besides all these, nanotechnology considered as the simple and finest approach in heavy metal removal with cost-effective, no further pollutant end-products and an environmentally friendly way (Azimi et al., 2017).

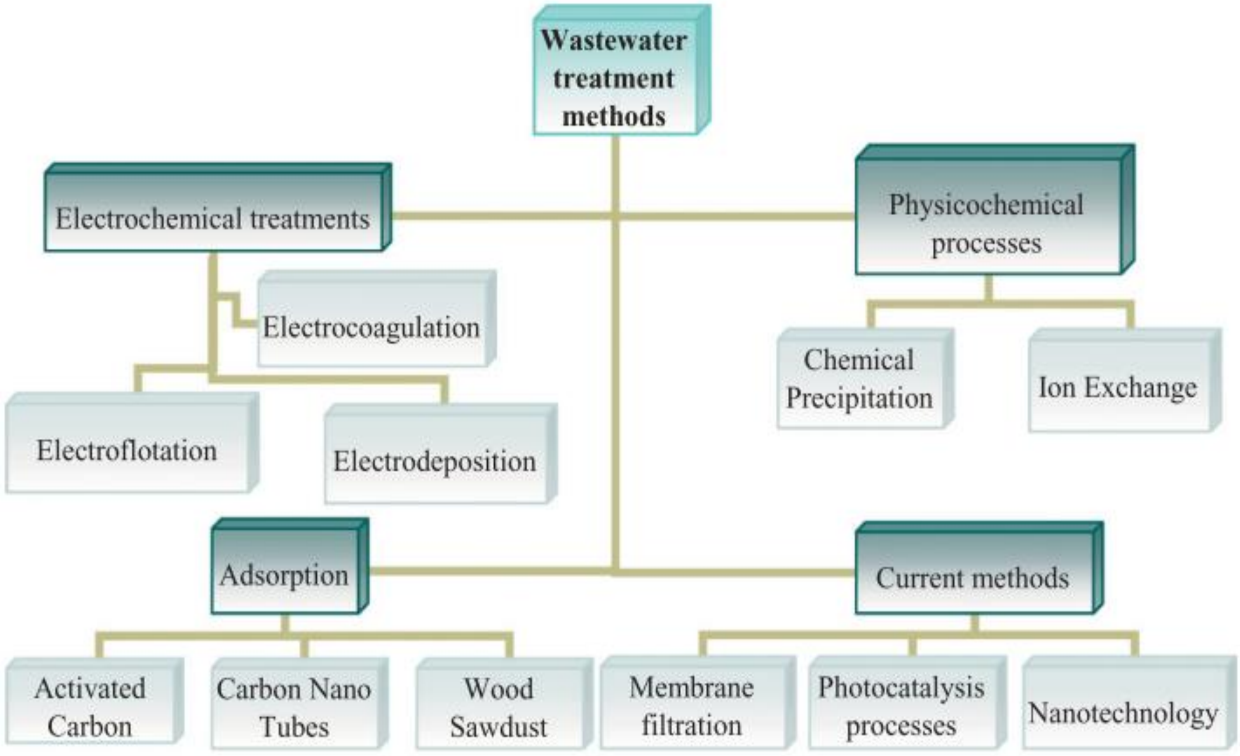


Figure 2.3: Techniques for Wastewater Treatment (Azimi et al., 2017)

Following are the major technique foe wastewater treatment.

- Chemical-Precipitation
- Electrochemical Treatment
    - Electrocoagulation (EC)
    - Electro flotation (EF)
    - Electrodeposition (ED)
- Membrane Filtration
- Electro-dialysis (ED)
- Flotation
    - Dissolved Air Precipitation (DAF)

    - Ion Flotation
    - Precipitation Flotation
- Coagulation Flocculation
- Ionic-Exchange
- Adsorption
    - **Nickel Ferrite Nanoparticles as Adsorbent**
    - Carbon Nanotubes Adsorbents
    - Activated Carbon (AC) Adsorbents
    - Low-Cost Adsorbents
    - Agricultural Wastes
    - Industrial Byproducts
    - Natural Substances
    - Bio-sorbents
    - Algae, Bacteria, Fungi
    - Eggshells, Banana Peels, Potato peels
    - Zeolite Clay etc

All methods of water and wastewater treatment for metals removal having their advantages and disadvantages. Traditionally, the Chemical – precipitation method is simple but Cost ineffective even at a low concentration of metal ions and produces a large amount of sludge that cannot be easily treated. Ionic exchange is a most common technique wastewater treatment, this technique requires a high cost for the treatment and not applicable for major scale project(Azimi et al., 2017).

Electrochemical method for wastewater treatment is a well fine and fast method that needs fewer chemical and generate less amount of sludge. However, this method required high electricity and high initial cost. The membrane filtration method is the most advance and high removal efficiency of heavy metals, but this method requires high initial, maintenance and membrane fouling and cleaning costs. this method has many limitations and restrictions in its development (Azimi et al., 2017 and Husnain., 2015).

Flotation technique having many advantages compared to other techniques such as metals selectivity, better removal efficiency, low detention periods, high overflow rates and produce a high amount of sludge. But high initial, maintenance and operating costs. Coagulation and flocculation for wastewater treatment requires high chemical consumption and high sludge production (Husnain., 2015).

Through most of the methods are cost-ineffective, required a high amount of energy and generate a large amount of sludge of toxic byproducts which cannot be easily treated, But adsorption is the safest, easiest, cost-effective and ecofriendly treatment technique (Tripathi et al., 2015; Hariharan et al., 2017 and Barakat et al., 2011). Most of the adsorbents are low cost including Nickel ferrite NPs and high efficiency for heavy metals removal and removal efficiency depend upon type and nature of adsorbent and this method is not applicable only in lab-scale but also used in field tests to remedy the groundwater in situ shown in below diagram (Yang et al. 2019 and Wang et al., 2012).

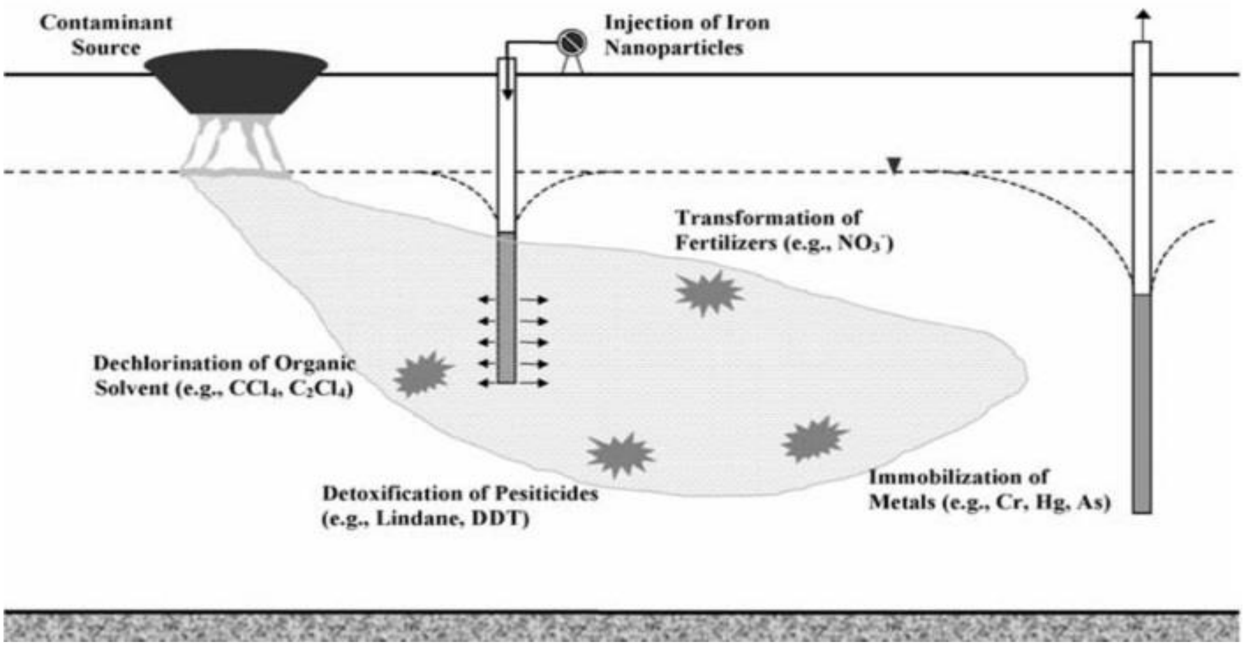


Figure 2.4: Nanoparticles for Groundwater In situ Remediation (Yang et al., 2019)

2.8. Advantages and Disadvantages

Conventional wastewater treatment methods with various processes include physical, chemical and biological processes having some disadvantages and limitations because of high investment cost, chemicals requirements, poor treatment efficiency (Zekić et al. 2018) time-consuming, huge sludge generation and required high cost for maintenance. However, the adsorption with nanoparticles is the most suitable and considerable method due to cost-effective, high metals removal efficiency and free from sludge formation (Manimozhi et al., 2016).

Nanoparticles for wastewater treatment is the most attractive method now a day due to the magnetic and chemical nature of produced sludge and ease of its disposal (Sagadevan et al., 2017 and Ong et al. 2012). they are chemically most stable and inert to the environment (Syam et al., 2014). Nanomaterial in wastewater treatment having many advantages includes.

i) The nano adsorbents themselves are non-toxic.

ii) Pollutant (adsorbed) can be easily recovered from nano-adsorbent surface.

iii) The adsorbents can be recycled and reused many times.

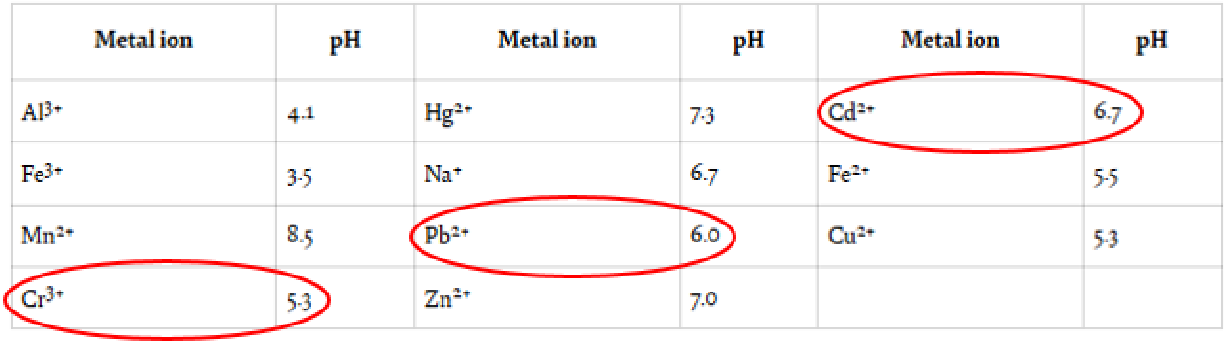
iv) NP's is sustainable and clean technology

v) Heavy metals can be separated from the nanoparticle's surface by desorption.

2.9. Adsorption onto NFN's

Recently, several approaches have been reported that NFN's is more efficient & ecofriendly treatment techniques for wastewater treatment (Renu et al., 2017) because of easiest, nontoxic, time-saving, low contact time, high reactivity and cost-effectiveness characteristic. Nanoparticles are those things that have small in size less than 100nm, Nanoparticles have been reported best option because of their small size and their unique mechanical, physicochemical and magnetic properties as by nature different from conventional materials. (Lu et al., 2019 and Husnain et al., 2015).

Due to magnetic properties NFN's as adsorbent make physical bond between bonding between nanoparticles and heavy metals depending upon the nature of intermolecular interactive force, this process called solid-liquid mass transfer. This adsorption method can be batch, semi-batch, or continuous (Tripathi et al., 2015).



Metal ion	pH	Metal ion	pH	Metal ion	pH
Al^{3+}	4.1	Hg^{2+}	7.3	Cd^{2+}	6.7
Fe^{3+}	3.5	Na^{+}	6.7	Fe^{2+}	5.5
Mn^{2+}	8.5	Pb^{2+}	6.0	Cu^{2+}	5.3
Cr^{3+}	5.3	Zn^{2+}	7.0		

Figure 2.5: Acidic Nature of Heavy Metals in Solution

Many researchers working on nanoparticles to enhance their properties to improve their efficiency, economic viability and other features, the following three types of nanomaterials are most researched nowadays:

- Nano adsorbents
- Nano membranes
- Nano catalysts

Nanomaterials and their applications must be commercialized at a small or large scale, but due to different points of view such as production cost, metals recovery cost, impacts on environment and ecosystem, etc are important but at temporary considerations.

2.9.1. Effect of Contact Time

These nanomaterials are small in size due to this unique feature nanomaterials consist of high surface area compared to other absorbents. Minimum 30 minutes time intervals are required for proper interstation or making a physical bond between adsorbent and adsorbed for obtaining optimal conditions that are sufficient for both to come in contact with each other. At the starting phase metals are capable to remove by adsorbent because at this phase adsorbents having many free sites on them where the speed of collision increases. On another side, the removal HM’s enhanced with slow speed collision because metals find less an opportunity to move towards the absorbent as found less opportunity toward adsorbents surface (Dargahi et al., 2016) because it depends on the rate of mixing that affect the adsorption processes but in this study, the mixing rate was fixed under some constant range 250 rpm desorption is take place where at high mixing rates occur where some of the metals may remove from the adsorbent surface this process called desorption. At a low mixing rate, the adsorption efficiency decreased, in the beginning, the adsorption may be very high but after some interval, no further adsorption takes place on the adsorption process (Dargahi et al., 2016 and Haleem et al., 2018).

2.9.2. Effect of adsorbent Dose

As increase, the number of adsorbents in liquid solution the removal of metal ion increases at a high rate it means at the beginning due to the high free site or more free particles having large surface areas for metal ions contribute more opportunity by adsorbed on it and increase the probability of collision between both of them (Dargahi et al., 2016). Adsorption can have some limitations when increasing the dose of adsorbents, such as increased output of sludge and high cost of buying absorbents. Therefore the high cost of buying an adsorbent should be considered at a high dosage, which is why it cannot be assumed that the process is economically the best process in all situations, so that the best process can be influenced by several factors, not just one factor. Other considerations that may be considered are the economical method, the availability of materials, etc (Dargahi et al., 2016).

Removal of chromium with different adsorbent dosages in dichromate solution has been studied. As the adsorbent dosage increases from 10 to 30 mg keeping all the other parameters constant, the efficiency seen in increasing mode. It was also observed that aggregation of particles take place with a higher concentration of adsorbent dosage and due to which the efficiency of Cr (vi) removal was decreased (Haleem., 2018).

2.9.3. Effect of pH

In Adsorption process, power of play important role in adsorption process and its removal efficiency because it changes the full nature of the adsorbent in the solution. Removal efficiency as decreasing pH value due to protonation of hydrogen ion (H^+) in aqueous solution (Dargahi et al., 2016). Many researchers have reported that more ionic charged which causes repulsion between metal ions (adsorbed) and NP's (adsorbent). NP's surafce became positively charged at low pH values due to protonation and adsorption was enhanced due to electrostatic forces between the NP and the negatively charged $Cr_2O_7{}^{-2}$ and $HCrO_4{}^{-2}$ ions (Li et al., 2001). While $CrO_4{}^{-\ 2}$ ions prevailed in the solution at higher pH values and investigated that with the protonation of H^+ with increasing of removal rate of metal ions. The adsorption process of metal ions is controlled by different parameters and pH value is significant among them. Different pH values have been tested, keeping other experimental conditions constant, to check the adsorption. Effect of pH inversely proportion to removal rate as it decreases with an increase in pH (Haleem., 2018; Alguacil et al., 2018 and Giraldo et al., 2013).

2.10. Disposal and Recovery of Heavy Metals

After water and wastewater treatment the big task will be the handling of an end – waste includes nanoparticles that accumulate in waste sludge that can be handle and transport in many ways. In the domain of the water and wastewater treatment field, it has been completely ignored for the safe and proper disposal of toxic waste in line with environmental protection principles (Zekić et al., 2018). The danger linked with the temporary containment of hazardous toxic metal wastes, in a dump or any other incompatible approach that could not cause serious environmental issues of groundwater contamination, health issues of lung cancer, skin irritations and cause damage to aquatic life in case of leakage into water bodies, this limits the temporary containment disposal option for hazardous waste. After metals recovery sustainable sludge handling is an issue of grave concern. Incorporation of such sludge into cement provides a safe disposal option. Further, dilution and dispersion do not provide a proper technical solution for the handling of the toxic metal waste but just a legal solution. Chronic exposure to toxic metals causes severe health issues, including increases risks of skin and lung cancers. Therefore, recently, the most interesting option for the disposal of waste is encapsulating and incorporation the toxic metals by solidification or stabilization methods and to dispose of the treated toxic wastes in safe landfills. (Husnain., 2015).

Metals can be regenerated by the desorption method. High concentrated acid and base can be use as agents to separate adsorbed from the adsorbent surface and metal can be recovered when adsorbent exhausted (Mohan et al., 2007). Desorption and adsorbent regeneration process is very costly it cannot be considered at this level of research and restoration of adsorbent with original efficiency of recovered material so it is very difficult to talk that why most of the researchers were not discussed on desorption/regeneration. Only few attempts discuss on literature about handling and final disposal of hazardous wastes (Mohan et al., 2007)

1. Burning of hazardous waste is not good option because hazardous waste containing toxic nonvolatile material that cannot burn.
2. Heavy metals recovery is not easy or possible because of high processing cost and difficult to restore of initial state of recovered materials

Materials and Methods

3.1. Chemicals Used in the Study

Chemicals which were used for the preparation of nanoparticles are

a. Nickel Nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$)

b. Ferric chloride ($FeCl_3$)

c. Hydrochloric Acid (HCl)

d. Sodium Hydroxide ($NaOH$)

e. Potassium dichromate ($K_2Cr_2O_7$)

f. 1, 5-diphenylcarbohydrazide ($C_{13}H_{14}N_4O$)

g. Ethanol (C_2H_5OH)

h. Acetone (C_3H_6O)

i. Sulphuric acid (H_2SO_4)

j. Oleic acid ($C_{18}H_{34}O_2$)

3.2. Preparation of Nanoparticles by Co-precipitation Method

Nickel ferrite nanomaterial is often synthesized in a small amount of time using this method shown in flow diagram 3.1. Precipitation starts with the formation of small crystallites (nucleation). These small crystallites will grow into more stable and large particles (growth). Nanoparticles are produced when the nucleation process is fast and the growth process is slow.

There are two categories of reactions for the synthesis of an oxide. In the first oxide is produced directly and in the second a precursor is produced which then undergoes further processing like calcination and drying. The resultant metal hydroxides precipitate in water and Oleic acid is added. After proper filtration and washing are done to obtain the final product. Nanoparticles of ferrite obtained through this process are fine, pure and homogeneous. Particle size depends upon the pH of precursor and molarity of chemicals. The crystallinity of particles is affected by impurities and reaction rate. Growth rate, nucleation and supersaturation affect the particle shape size. Particle size has an inverse relation with supersaturation. Temperature and pH have an imperative important part in the precipitation process (Polshettiwar et al., 2018). the experimental procedure also is shown in below schematic diagram.

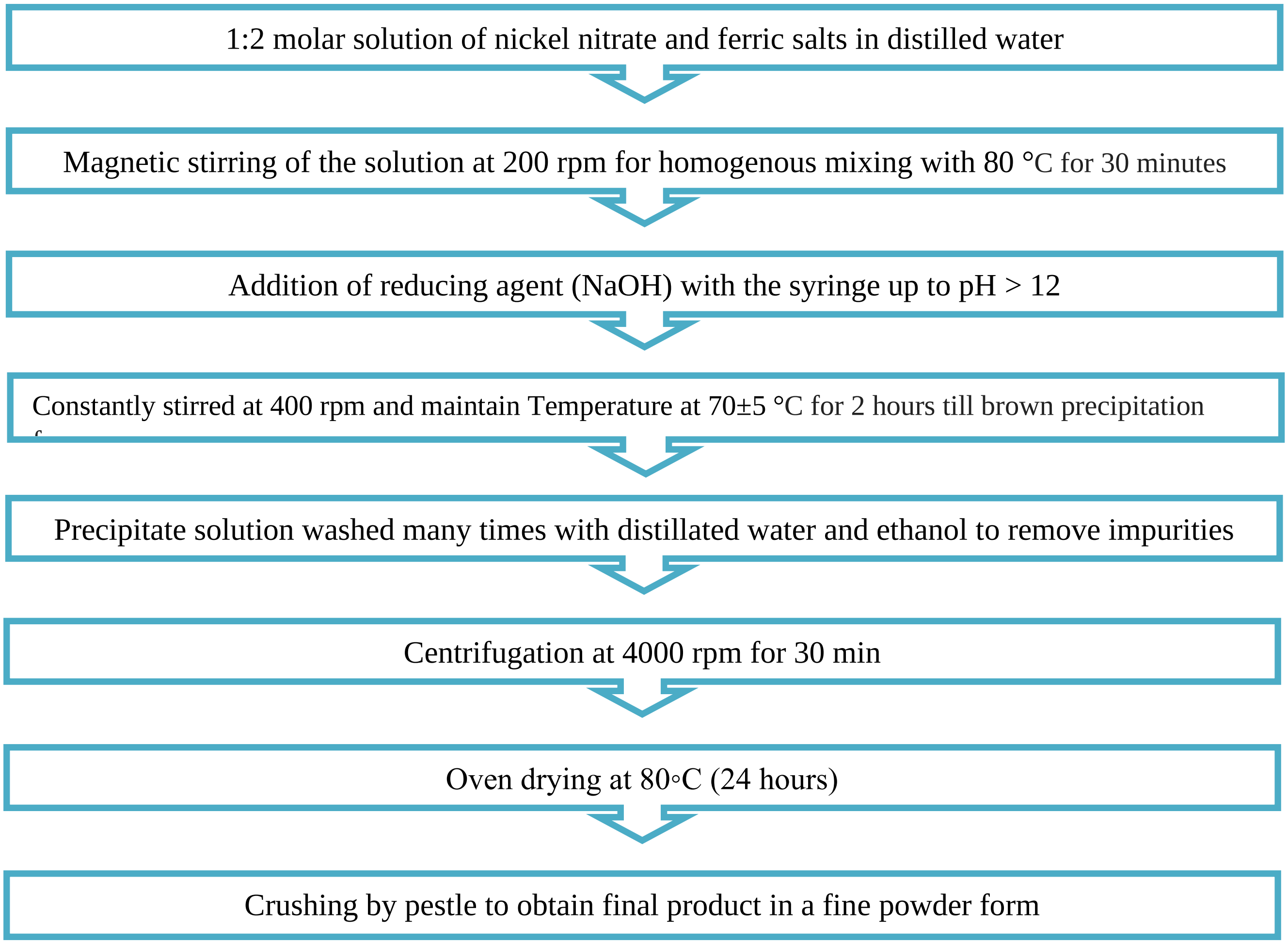


Figure 3.1: Flow Diagram foe Synthesis of Magnetic NFN's

3.3. Test Instruments

During the study following instruments were used

Filter assembly, pH meter (Cyber Scan 700 Eutech), Magnetic Stirrer (Corning PC 4200), Centrifuge (Hermle – Z206A), UV Spectrophometer (T – 60 PG Instruments), Atomic Absorption Spectrophotometer, Scanning Electron Microscope (JOEL JSM- 6490) and X-ray Diffraction (XRD JOEL JDX-II)

3.4. Important Parameters studied in the Co-precipitation Process

Some parameters are critical to control and optimize to achieve the desired results at the end of the co-precipitation process. They are explained below:

i) Mixing rate of reactants

The rate of mixing is an important parameter as it has direct effect on the nanoparticles size which are synthesize. When the mixing rate is slow, the nucleation rate is less than the growth rate and therefore, the particle size is larger. When the mixing rate is high, the nucleation rate is higher than the growth rate and therefore, we obtain particles of smaller size. However, the mixing rate must not be extremely high because in that case, the homogeneity of particles would be reduced.

ii) Temperature

The energy required to activate to transform reagent into production during a reaction is known as activation energy This energy is obtained by supplying heat during the reaction phase. Each metal has a unique value of activation energy for converting into ferrites. In the case of making nickel-based ferrites, the reaction temperature is usually kept at 70-80 °C.

iii) pH

Particles size and shape are greatly influenced by the values of the pH maintained during their synthesis. There is a negligible growth of particle size at low pH values. That is why a strong base like caustic soda gradually added drop wise to increase pH of solution for increase of particles size and their growth to a significant level. Moreover, the time taken to completion of the reaction is also reduced by increasing the pH. A pH range of about 8-9 was kept during the reaction in our experiment.

iv) Stirring time

It also has a significant effect on the particle size. Shorter stirring times lead to relatively larger particle size and insufficient homogenization of the particle composition. Longer stirring times at higher temperatures result in very fine particles and are convenient for obtaining nanoparticles during co-precipitation.

v) Heating after co-precipitation

When the dried ferrite powder is obtained, it is further calcinated at a high temperature for a certain time so that annealing would occur and a distinct spinal phase is obtained. Therefore, the temperature and the time for calcination is critical as it would change the size and morphology of the final powder particles.

vi) Role of anion

The type of anion used also influence the final properties of the powder particles synthesized. They can be present in various types i.e. as metal ion solutions or as metals salts. Better results are obtained when they are present in the form of metal salts. The possible salts that can be employed include nitrates, sulfates, or chlorides.

3.5. Preparation of NFN's

Co-precipitation method was used for the preparation of Magnetic NFN's. 2.91 gram of $Ni(NO_3)2.6H_20$ was dissolved in pure ultra-water to made 50 ml of 0.2 molar solution of $Ni(NO_3)2.6H_20$ and 5.406gram of Ferric chloride salt ($FeCl_3$)dissolving in distilled water to make 50mlof 0.4M solution of Ferric chloride ($FeCl_3$), both solutions are mixed properly in magnetic stirrer at 200 rpm for homogenous mixing with 75 °C for 30 minutes then place out for cool at room temperature, 12g of NaOH mix in 100 ml distilled water to made100 ml of 2 M solution of mineralizer sodium hydroxide (NaOH) and were added drop by drop with a syringe as precipitating agent up to the solution reach required pH (e.g:8,9) with constant stirred at 400 rpm and maintain the temperature at 70±5 °C for 2 hour till brown precipitation form and the solution pH was thoroughly and continuously observed, NaOH solution add dropwise at stirring 200rpm for 2-hours with 80°C. Afterwards, the obtained brown precipitate product was cooled at normal room-temp. and then product was washed several times for having neutral pH, ethanol was used at (C_2H_5OH) to eliminate unwanted impurities from sample and then placed in centrifuge device at 4000 rpm for 30 minutes to remove all excess impurities from our final product to get the pure final product, the obtained dried at oven with 70 °C for 24-hours and afterward the dried nano powder will ground and calcinated at 350 -550°C for 3-hours at muffle furnace device to obtain pure $NiFe_2O_4$, crushing by pestle to obtain the final product is a fine powder form. To prepare the nanoparticles nickel and ferric chloride salts are mixed in 1:2 molar ratios.

$$Ni\ (NO_3)_2{\cdot}6H_2O\ (1\ mol) + FeCl_3\ (2\ mol) \rightarrow Ni\text{-}Fe_2O_4\ (3mol)$$

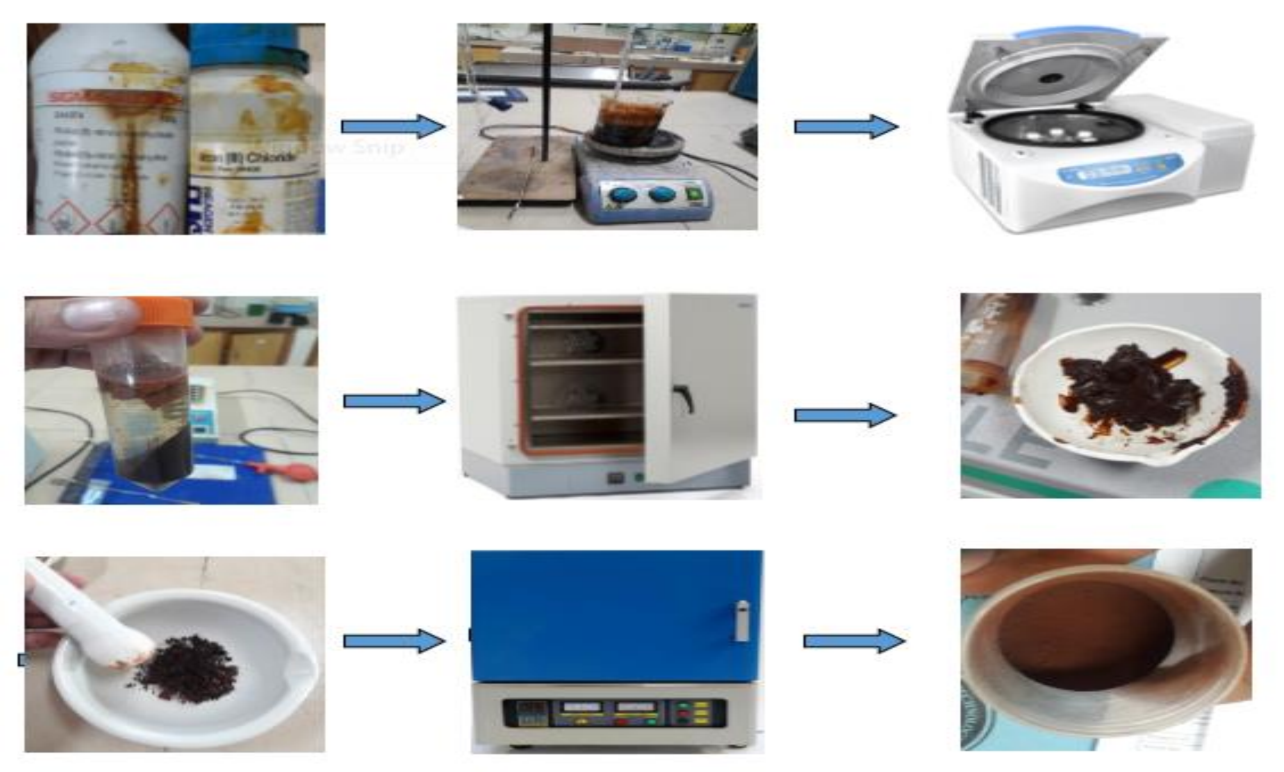


Figure 3.2: Steps Involved for the Synthesis of NP Nanoparticle

3.6. Characterization of Nanoparticles

Determination of the surface properties of the synthesized nickel-ferrite nanoparticles was carried out by Scanning Electron Microscope (JOEL JSM- 6490). The elemental constituents were further determined by using Energy Dispersive spectroscope JED-2300 model and X-ray Diffraction (XRD JOEL JDX-II) model was used to determine and investigate size and crystallinity structure of prepared nanoparticles.

3.6.1. X-ray Diffraction

X-ray Diffraction (XRD JOEL JDX-II) technique was conducted for the determination of the crystallinity structure and overall size of NP’s. Scherer formula was used for calculation of crystalline size (Younas et al., 2014). XRD Working mechanism is as shown in Figure 3.3 in which the x-rays fall on the specimen atoms and diffracted into many directions.

$$L = K\lambda / \beta \cos\theta$$

Whereas,

L = Average size of nanoparticles, k = 0.8; λ =0.15, β = dFWHM, θ = diffraction angle.

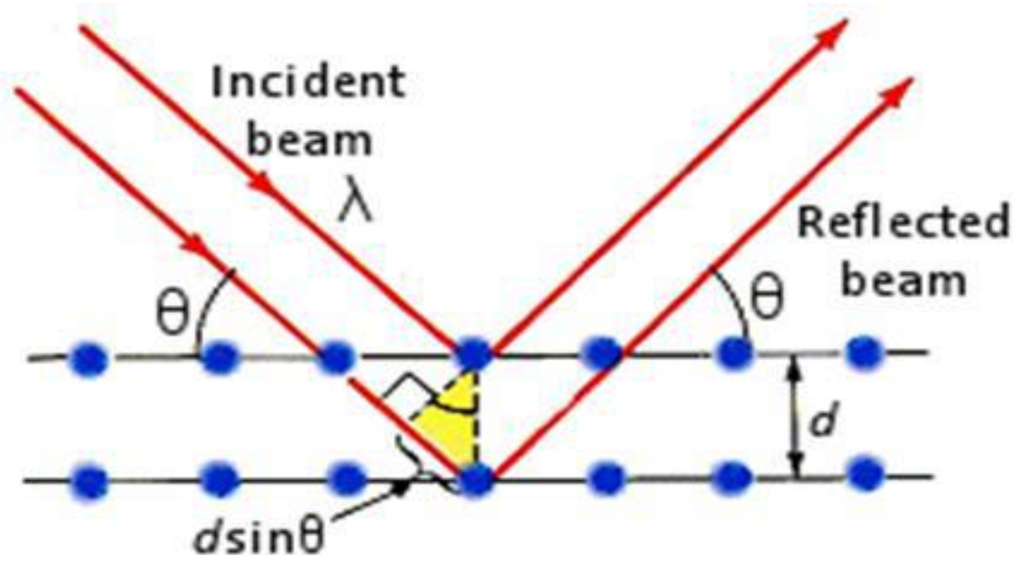


Figure 3.3: XRD Working Principle

- The composition of the crystal defines the atomic arrangement of the substance.
- The crystal structure specifies the location and strength of the diffraction peaks of the X-ray scattering pattern.
- Due to scattering of light parallel to objects/atoms make diffraction peaks
- The Miller indices (hkl) are used to identify the different atom planes.
- Diffraction peaks make with objects/atoms plane that make easy to analyze of sample (Banerjee et al., 2018).

3.6.2. Scanning Electron Microscope

SEM technique was used for determinations of surface structure of NFN's which utilizes a concentrated beam of electron to obtain large-magnified image. Information is given by high-resolution, three-dimensional images generated by SEM.

- Topography
- Morphology
- Chemistry
- Crystallography

This technique was used to find out the topography and morphology of the Nickel-ferrite nanoparticles (NFN's), at 50,000 and 10,000x magnifications and for estimation of nanoparticle size and examination of powder sample. It has a resolution of 0.5 - 10 µm. X-rays informed us about the elemental and chemical composition of the sample as shown in Figure 3.4 (Goldstein *et al.*, 1981).

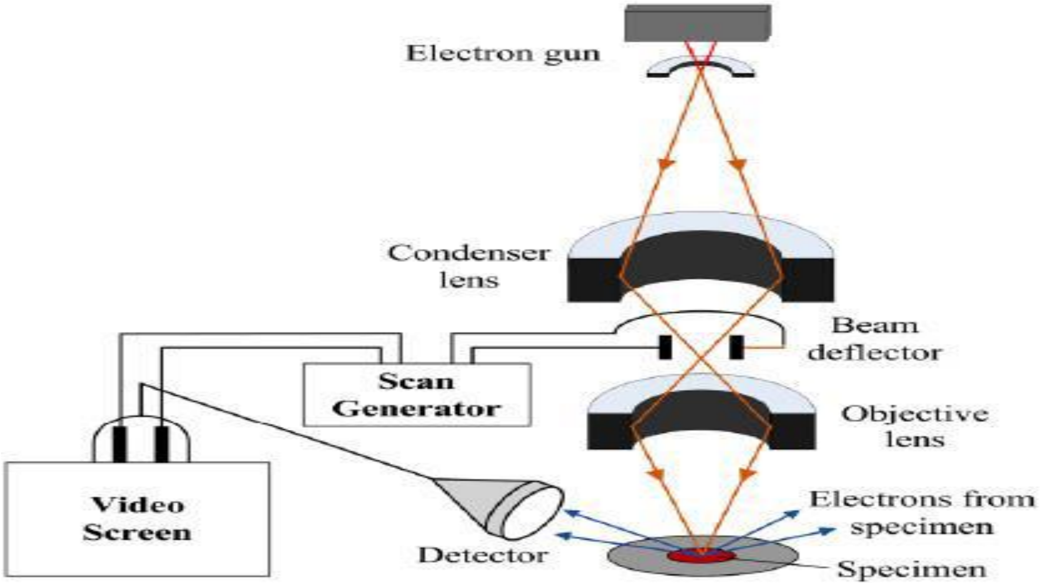


Figure 3.4: SEM working Principle

3.6.3. Energy Dispersive spectroscopy

EDS technique was used for the determinations of elemental composition of the selected region of sample and relative mass. The principle of EDS is shown in Figure 3.5. which involves the electron beam which falls on the sample atom. Due to the excitation in the inner shell of an atom, every element produces x-rays. This moves the outer shall electrons to move towards the inner shall cover the gap. Xrays are emitted when difference in an outer and inner shell occurs. These x-rays form the specific peaks for each element which is detected by EDS. Thus, the controlled beam of an electron can also tell us about the elemental composition of a selected area (Goldstein et al., 2003).

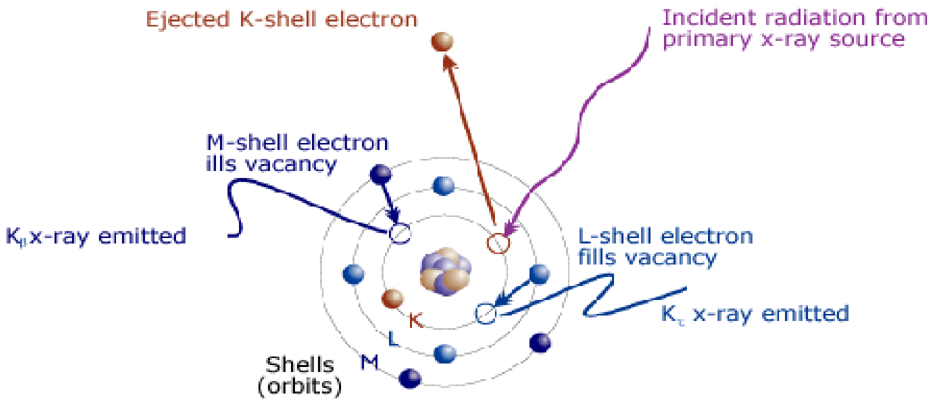


Figure 3.5: EDS Working Principle

Element	Weight%	Atomic%
O K	25.79	44.79
Na K	18.22	22.03
Cl K	18.96	14.86
Fe K	32.69	16.27
Ni K	4.34	2.06
Totals	100.00	

3.7. Sample preparation

3.7.1. Synthesis of Standard Solution of Chromium

Preparation of Cr (VI) stock solution of 5 mg L-1 involves dissolving 0.1414 gram potassium dichromate (K2Cr2O7) in distilled water and diluting to 100 mL; 1.00 mL = 500 µg of Cr. 5 ppm Cr (VI) solution was synthesized at the lab by diluting pure water with a stock solution and creating a standard chromium solution of 5 mg/L.

The stock solution was diluted further to prepare standard stock solution of 0.05 mg/L; these two stock solutions were used to prepare Cr (VI) standards for the calibration curves with the following concentrations: 0.5, 1.0, 2.5, 3.5 and 5µg/L. The chromogenic reaction of the chromate solutions was allowed to equilibrate at room temperature (30°C). The Diphenylcarbazide reagent used for Cr (VI) water analysis was added to the calibration curve solutions since the reagent is hygroscopic and deteriorates with time. The analysis solutions were mixed by hand for a few minutes until completely dissolved. Incomplete mixing does not provide a proper chromogenic reaction and will affect the absorbance values obtained for the reagent reaction. The chromogenic reagent was added to the solution right after opening, mixed for one minute and the reaction time at the absorption maximum of 540 nm was measured. The chromogenic reaction was completed 2 minutes after starting the time-based measurement (3 minutes after the addition of the reagent). Further, the reagent color became stable 10 minutes after starting the measurement (5 minutes after the addition of the reagent).

3.7.2. Preparation of Lead Stock and Standard Solution

Following the same procedure (3.5 Preparation of chromium stock solution) for preparation of lead stock solution by dissolving 0.15985 g of Lead Nitrate ($Pb(NO_3)$) in distilled water and dilute to 100 mL to prepare ; (1.00mL = 5 ppm of Pb). The solutions with 5ppm concentrations of lead were prepared by dilution of the stock solution with ultrapure water, producing a 5 mg/L lead standard stock solution of 1000 mL. This was further diluted to create another standard stock solution of 0.5 mg/L (10mL = 0.5 ppm of lead); this stock solution was used for adsorption experiments.

3.7.3. Preparation of Cadmium Stock and Standard Solution

Preparation of cadmium stock solution by dissolving 0.2744 g of Lead Nitrate (Pb (NO_3)) in distilled water and dilute to 100 mL to prepare. The solution with 5ppm concentrations of cadmium was prepared by dilution of the stock solution with ultrapure water, producing a 5 mg/L cadmium standard stock solution of 1000 mL. This was further diluted to create another standard stock solution of 0.5 mg/L; this stock solution was used for adsorption experiments.

3.8. Analytical techniques for the quantitative determination of heavy metal

3.8.1. Spectrophotometric Determination of Chromium

UV/Vis spectrophotometer technique was used for the detection and quantization limits of Cr (VI), this instrument (HACH DR 2400) detect the absorbance rate at λ_{max} 540 nm, Calibration curves were created using reagent manufacturer for simple quantitative determinations as shown in figure 3.6.

Figure 3.6: UV Spectrophotometer for the Quantitative Determination of Cr (VI)

3.8.2. Working Principle of Spectrophotometer

The instrument calculates the transmitted light, which is generally referred to as transmittance. Samples are placed to light measurements and some percentage light passes through solution and transmits a voltage signal to the monitor. If the absorption of light increases, the voltage signal changes as well (Thomas et al, 2007).

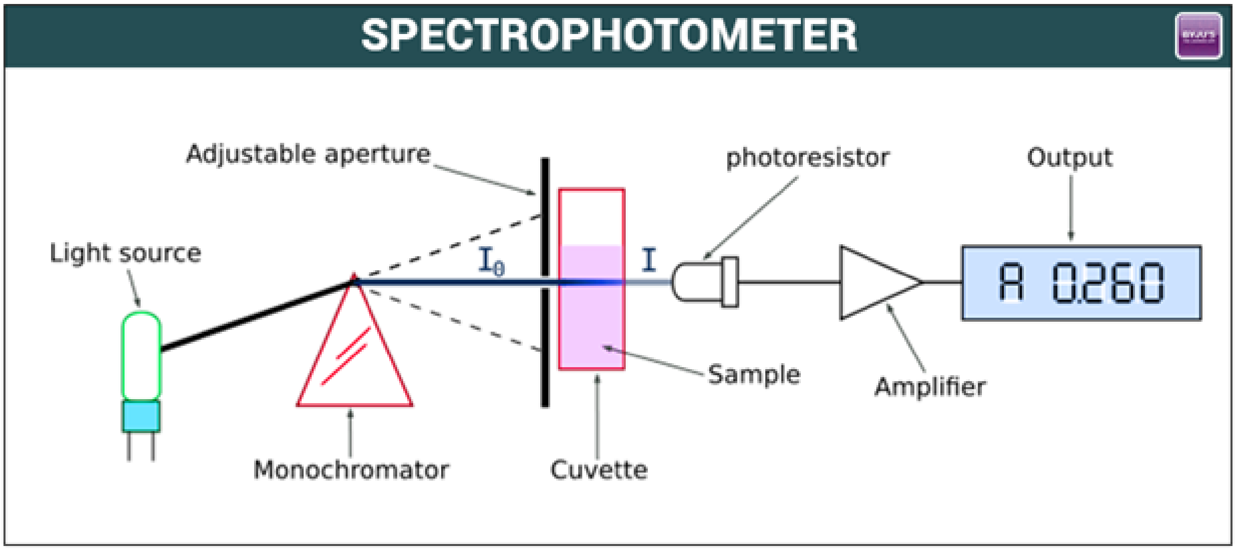


Figure 3.7: Working Principle of Spectrophotometer

Every element absorbs and or reflects light of a certain wavelength. So, this instrument calculates that how much an element absorbs or transmits the light.

3.8.3. Preparation of Calibration and Standard Curve

UV-Visible spectrum of a dye Diphenylcarbazide (DPC) was recorded for determining Cr (VI) in synthetic wastewater to validate at λ-max 540 nm with sample of different concentration from 0.5µg/l to 5 µg/l, which follows the standard method as shown in Figure 3.8.

The standard method (3500 Cr) was used for the detection of Cr concentration through UV Spectrophotometer at 540 nm. Following chemicals were used for sample preparation.

1. 50 ml of prepared stock solution of 5ppm (synthetic Cr (vi) solution)
2. 50% Sulphuric-acid of (0.5 ml) was used for adjusted pH 2.0±5
3. Phosphoric acid, H_3PO_4 (0.25 ml) - 3 drops
4. 1, 5-diphhenylcarbazide solution (2 ml) in ultra-pure water
5. Solution volume adjusted to volumetric flask of 100ml
6. Shake well till color develop before placing the sample in UV-Visible spectrophotometer

141.4 mg potassium dichromate chemical was added into ultra-pure water of 100mL of flask to make 5ppm solution. DPC solution was prepared by adding of 250mg of 1,5 Diphenylcarbazide into 50mL volume of acetone. Sulphuric acid were used for the adjustment of pH then using prepared chromium solution of 0 - 1.0mg/l with DPC solution. The standard chromium solution (0.005 mg/L or 5µg/L) were used to make serial dilution of 2- 20 ml solutions So that why dilute of the stock solution up to the range, were prepared 5 sample $S_{1,}$ $S_{2,}$ $S_{3,}$ S_4 & S_5 of different volume 1, 2, 5, 7 & 10 mL respectively of a 5 µg/l Cr and pH were adjusted to 2.0±5. Transfer of solution to 100 ml volumetric flask and were adding three drops of Phosphoric acid (H_3PO_4) plus adding of 2 mL of prepared 1, 5-diphhenylcarbazide solution and mixed till the color appeared. Afterwards samples placed in UV spectrophotometer for analyzed at max. wavelength of 540nm.

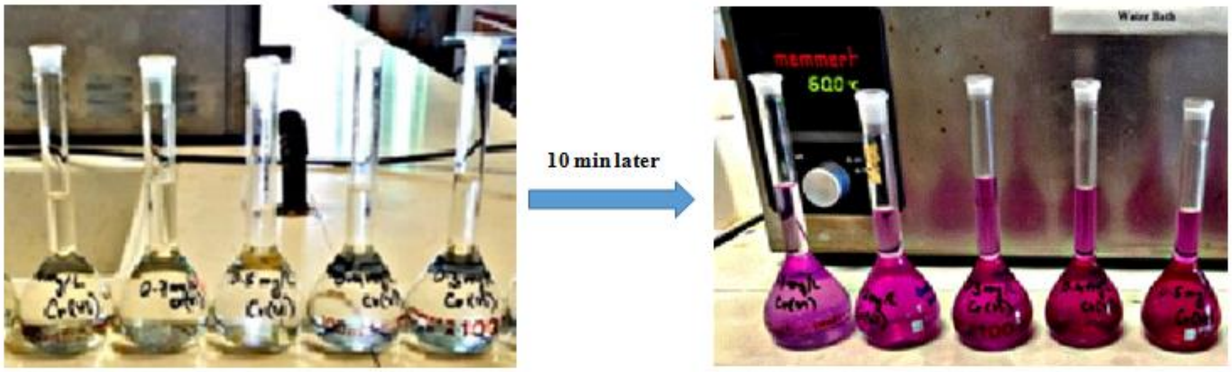


Figure 3.8: Five Standard Samples for Preparation of Calibration Curve

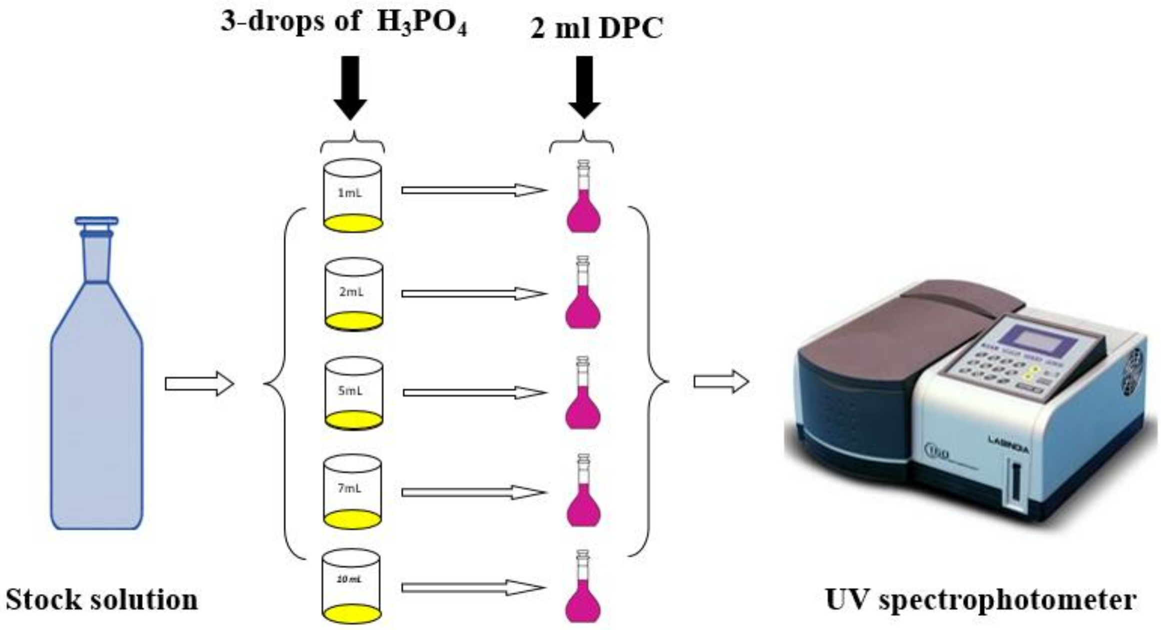


Figure 3.9: Steps for Preparation of Standard Calibration Curve

Table 3.1: Absorbance Values with Different Volume of 5 µg/l Cr (VI) at 540 nm

Samples Run	Volume (mL)	Absorbance (@540 nm)	Concentration (µg/l or ppm)
S_1	1	0.068	0.5
S_2	2	0.119	1
S_3	5	0.241	2.5
S_4	7	0.33	3.5
S_5	10	0.462	5

3.9. Adsorption Experiment - Batch Method

Adsorption studies were carried out by mixing 10, 20, 30, 40 & 50 mg of NFN's with 50 mL synthetic wastewater of Cr (VI), Pb (II) & Cd (II) solutions of 5ppm in 100 mL backer. The solutions were agitated at 200 rpm over different contact time (30, 60, 90 &120). The pH values of synthetic wastewater solutions were adjusted to 3.0–7.0 by using 1.0M HCl and 1.0M NaOH solutions. Effect of Adsorbent dosage was determined and pH value of 3 and the initial Cr (VI) were used. An acetate membrane filter of 0.22 um thickness was used to separate the aqueous phase. UV-Visible spectrophotometer was used to find out the concentration of Cr (VI) in the filtrate solution.

The Cr (VI) solution of 5 ppm was synthesized at the lab by dilute distilled water. Adsorption procedure was carried out with dosage 10, 20, 30, 40 & 50 mg of Ni-Fe_2O_4 adsorbent with 50 mL Cr (VI) solutions of 5 ppm. The solution was mixed over a magnetic stirrer at 200 rpm with different pH and contact time, 3, 4, 5, 6 & 7 and 30, 60, 90, & 120 min, respectively. The solution pH was adjusted by using strong acid and base (HCl and 1 mol L^{-1} NaOH) as reagents.

Table 3.2: Experimental Parameters for Adsorption

pH	**pH is maintained at levels (3, 4, 5, 6 & 7)**			
Adsorbent Dose (mg) Applied at each pH level	**10, 20, 30, 40, 50**	**10, 20, 30, 40, 50**	**10, 20, 30, 40, 50**	**10, 20, 30, 40, 50**
Contact Time (min)	**30**	**60**	**90**	**120**

Adsorption experiment was done by measuring 50mL of the synthetic wastewater sample and poured into a 100mL Backers. 10, 20, 30, 40 & 50 mg of the synthesized nickel nanoparticles were added to different backers containing 50mL of synthetic wastewater. The backers containing the adsorbent and the synthetic wastewater were placed on a magnetic stirrer at 200 rpm at room temperature for a period of 120min to ensure equilibrium. The suspension was filtered using 0.22-micron filter paper. UV/Vis and Atomic adsorption Spectro-photometer (AAS) was used to analyze the concentration of the different metal ions present in the filtrate.

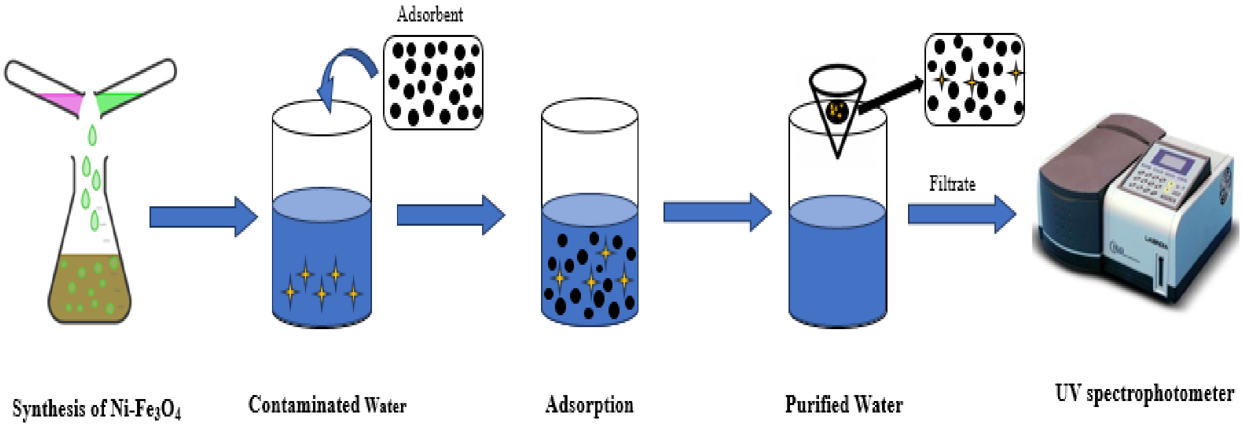


Figure 3.10: Purification Process of Contaminated Water Through Adsorption

The effect of pH on the adsorption of metal ions in the pH range of 3-7 was studied under the specific condition (Temp = 30 °C, agitation speed = 250rpm, adsorbent dose = 10 mg and contact time = 90 min). Adsorbent dosage was varied from 10 to 50 mg, under the specific condition (contact time of 90 min, 250 rpm shaking speed and pH of 3 - 5 at room temperature) using nickel ferrite nanoparticles. The number of metal ions adsorbed by the adsorbent was evaluated and the following formula was used to calculate the percentage removal.

$$E = C_o - C_e / C_o * 100 \text{----------} (1)$$

Where (E %) is the ratio of the difference in metal concentration before and after adsorption.

3.9.1. Effect of Contact Time

The effect of contact time on the removal of metal ions was studied for the interval of 30 minutes up to 120 minutes. 10 Mg of the nickel ferrite nanoparticles NFN’s adsorbents were added to separate backers containing 50mL of wastewater. The backer was closed and placed in a rotary shaker and agitated at speed of 200 rotation per minute (rpm), for each of the different contact times chosen (30, 60, 90 and 120 min). The content of each backer was filtered and analyzed using UV/Vis and Atomic Absorption Spectroscopy after each agitation time

3.9.2. Effect of Adsorbent Dosage

Different dosages of the adsorbents (10 – 50 mg) were added in different backers containing 50mL of synthetic wastewater solution, corked and agitated in a shaker for 180 min at a speed of 200 rotations per minute (rpm) at a room temperature of 30 °C. The content of each backer was then filtered and analyzed using UV and Atomic Absorption Spectroscopy after agitation time.

The percentage removal increased with the increase in dosage. This occurred until an optimal dosage of 30 mg of Cr (VI), 40 mg for Pb (II) and Cd (II) was reached after which the removal was the same. Starting from 10 mg with an increment of 10 mg, the dosage was increased up to 50 mg showing increase removal with increased dosage until the maximum removal is achieved at 30 mg which is the optimum dosage for removal of Cr (VI), 40 mg for Pb (II) and Cd (II). Increasing the percentage of adsorption with adsorbent dose may be due to the increase in adsorbent surface area and the availability of more adsorption sites. The rate of adsorption, however, decreased with an increase in adsorbent dose after the optimal value. This is maybe due to the overlapping of adsorption sites as a result of overcrowding of adsorbent particles.

3.9.3. Effect of pH

The effect of pH on the adsorption of metal ions in the pH range of 3 - 7 was studied. For this investigation, 50 mL of synthetic wastewater was taken into different 100 mL backers and 10 mg of the nickel ferrite nanoparticles NFN's were added and agitated at a speed of 200 rpm for 30 to 120 min. The 0.22-micron filter paper was used to filter the mixture and the filtrate was analyzed to determine the concentrations of metal ions using UV/Vis Atomic Absorption Spectroscopy.

Results and Discussion

4.1. Synthesis of Nickel-Ferrite Nanoparticles

In the co-precipitation technique, an appropriate amount of ferric nitrate and nickel nitrate were dissolved in de-ionized water. Magnetic Nickel-ferrite nanoparticles (NFNs) were synthesized using co-precipitation method at 70±5 °C followed by calcination at 350-550 °C kept under constant stirring, in order to control the pH and annealing temperature because the size and shape of the nanoparticles formed is greatly influenced by the pH and purity of synthetic nanoparticles depends upon annealing temperature and molarity of chemicals. Co-precipitation derived particles had homogeneous & spherical shape and very small particle size with a wide size distribution.

4.2. Structure Studies

Characterization tools were used to confirm the Nanostructure of NFN’s. One of these techniques is X-ray Diffraction (XRD) was used to find out the crystalline structure and size of nanoparticles. The surface properties of synthesized nickel-ferrite nanoparticles were determined using Scanning Electron Microscopy JEOL, JSM 6490A, Japan. The elemental composition was further confirmed using Energy-dispersive spectroscopy (EDS, JEOL JSM 6490A).

4.2.1. XRD analysis

X-ray diffraction patterns of co-precipitated and calcined nickel ferrite nanoparticles are shown in Figure 4.1. X-ray diffractometer (Theta/Theta STOE Jeol Germany) with monochromatized CuKa was used to obtain X-Ray diffraction patterns of Nickel ferrite. The measurement was performed in the range from 20° to 80°. XRD spectrum of the prepared sample was investigated in order to confirm the formation of synthesized nickel ferrite nanoparticles. Furthermore, it was observed that XRD patterns are well-matched with the standard diffraction data JCPDS No: 03-0864 to confirm the face-centered cubic spinel structure of synthesized Nickel ferrite. It has been shown that the synthesized sample has a spinal cubic structure. The NFN's contained no impurity peaks within the limit of X-ray detection. The significant peak broadening indicates the ultra-fine nature of the sample. The average crystalline diameter (D) was calculated by Scherer's equation,

$$\mathbf{D=0.9\lambda/\beta\cos\theta}$$

Where D is the crystallite size, β is the line broadening at the full width at half maximum (FWHM) of the most intense peak, K (0.9) is Scherrer constant, θ is the Bragg angle and λ is the X-ray wavelength. The average crystalline size of nickel ferrite nanoparticles was calculated as 30.254 nm.

Table 4.1: Determination of Particle Size

Peak Positions (2 Theta)	Full Width at Half Maximum (FWHM)	Crystalline Size D (nm)	Diameter (nm) (Average)
27.29386	0.23616	34.617	**30.254**
29.84807	0.94464	8.703	
31.63629	0.15744	52.445	
45.37836	0.1968	43.753	
53.90006	0.94464	9.434	
56.43597	0.23616	38.176	
66.19782	0.47232	20.077	
75.2411	0.288	34.825	

The peaks shown in the XRD pattern of Nickel ferrite are intense and sharp, representing good crystallinity of the prepared sample. In Figure 4.1. the peaks were found to be at 2θ values of 29.84807, 31.63629°,35.27°, 45.37836°and 56.43597° corresponded to the crystal planes of (220), (311), (222), (400) and (511) of Nickel ferrite, that confirms the formation of NFN's spinel phase. No other peaks are observed, indicating that the synthesized sample consists of high-purity NiFe2O4.The average crystalline size of nickel ferrite nanoparticles was calculated as 30.25 nm as shown in table 4.1.

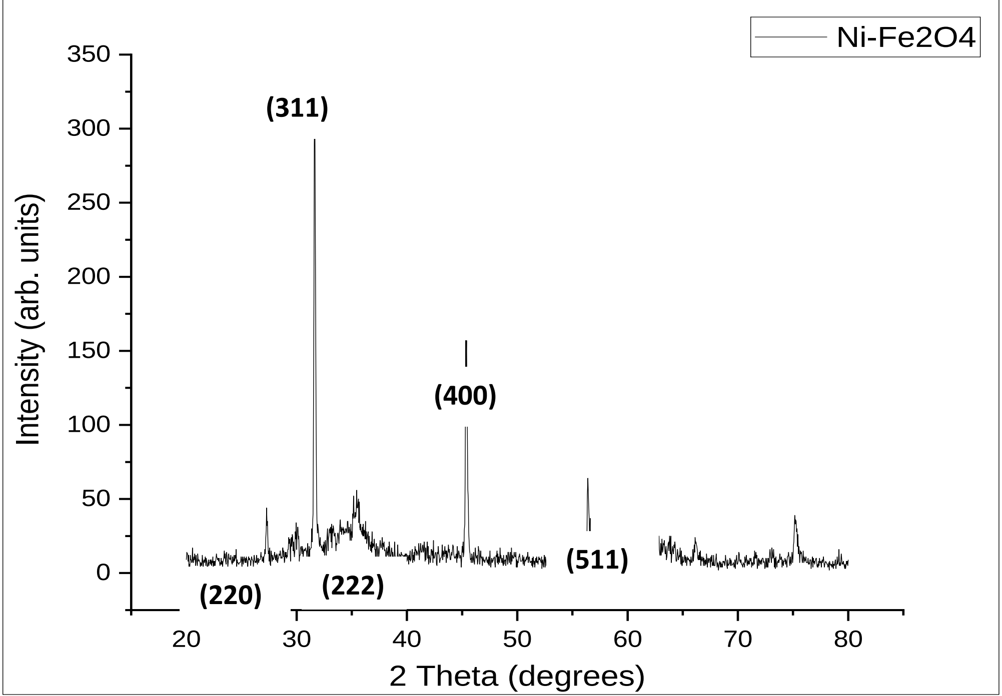


Figure 4.1: XRD Pattern of Nickel-Ferrite Nanoparticles.

4.2.2. SEM analysis

Scanning Electron Microscope (SEM) with high resolution is an influential instrument for imaging of fine structures of nanoparticles. SEM (Jeol JSM-6490A, Japan Analytical scanning electron microscope) was used to study the surface morphologies of the samples. The sample was coated with a thin layer of conducting material (gold) and was imaged at ×2,000 ×3,000, ×20,000, ×30,000 magnifications. The accelerating voltage was 10 kV. A focused high-energy beam of electrons interacted with the surface of the sample and generate secondary electron, backscattered electron and characteristic X-rays signals. These signals were perceived by the detector and images were displayed on the cathode ray tube screen. Scanning electron micrographs of the synthesized NFN's is shown in figure 4.2. It was observed that the substance was a homogeneous & spherical shape with uniform size distribution. It was also confirmed that the particles are not aggregated. The average size of synthesized NFN's at × 30,000 magnifications was 60 - 80 nm as shown in figure 4.2.

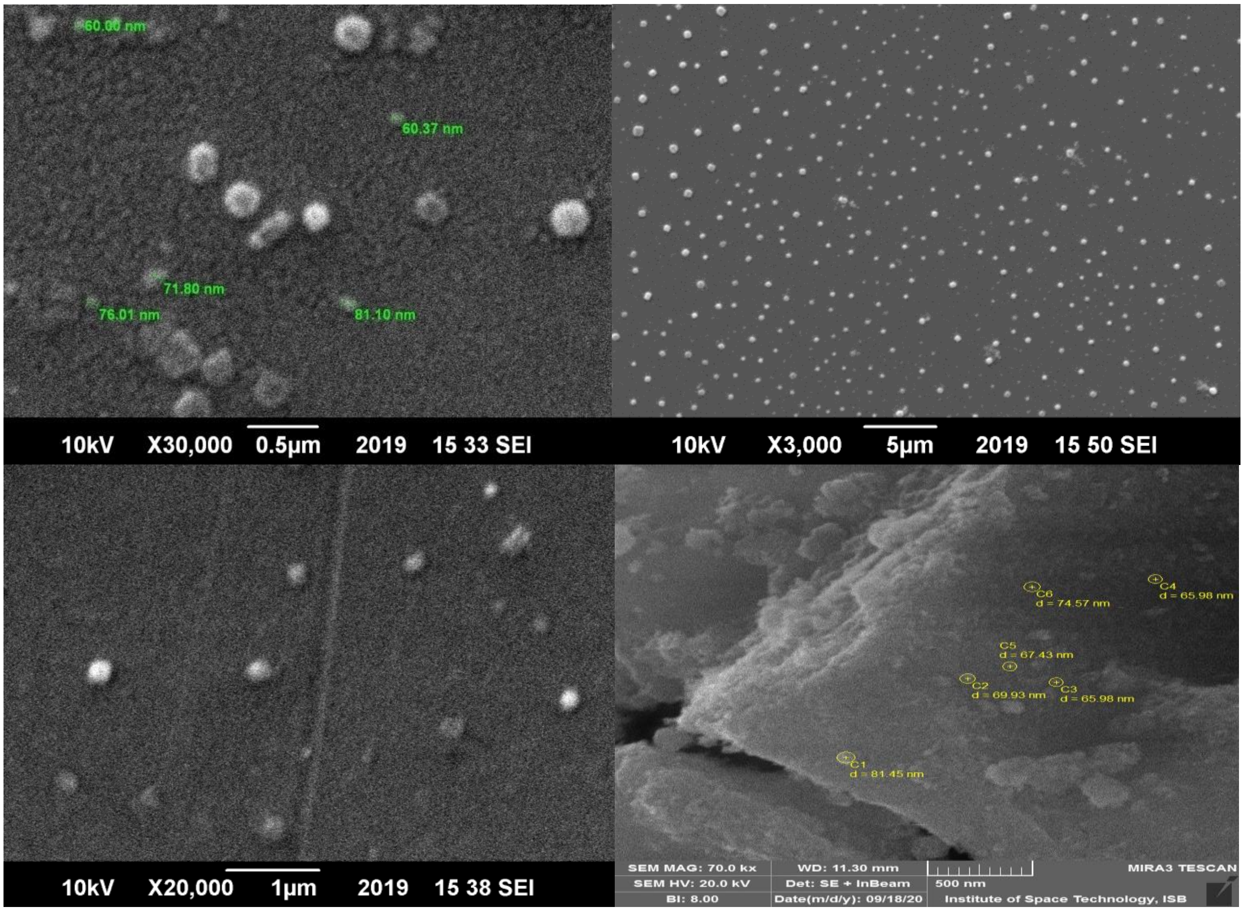


Figure 4.2: SEM Images of Nickel- Ferrite Nanoparticles.

4.2.3. Energy Dispersive Spectroscopy (EDS)

EDS is the technique used for the determinations of the elemental composition of a selected area and relative elemental mass of synthesized NFN's as shown in figure 4.3. The achieved results confirmed that different elements present in the NFN's sample, such as nickel, iron and oxygen, while other elements like chlorine and sodium were also detected because the salt of the elements was used in the study as shown in table 4.2.

Table 4.2: Relative Elemental Mass of Synthesized NFN's

Element	Weight%	Atomic%
O K	25.79	44.79
Na K	18.22	22.03
Cl K	18.96	14.86
Fe K	32.69	16.27
Ni K	4.34	2.06
Totals	100.00	

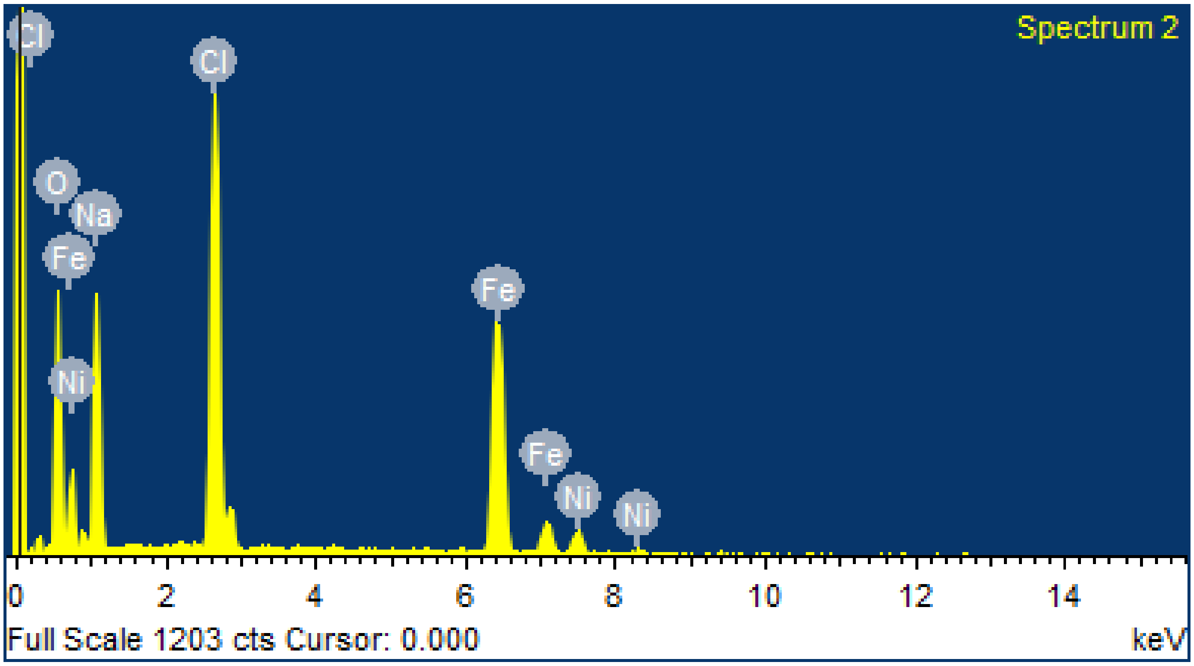


Figure 4.3: EDS of Nickel-Ferrite Nanoparticles

4.3. Absorbance Spectra of Diphenylcarbazide (DPC) to Determine Cr (VI)

Diphenylcarbazide (DPC) standard method (3500-CR) was used to determine Cr (VI) in synthetic wastewater using a UV-Visible spectrophotometer. For this reason, the spectrum of a dye Diphenylcarbazide (DPC) was recorded for determining Cr (VI) in synthetic wastewater to validate the wavelength of maximum absorbance of 540 nm, which follows the standard method.

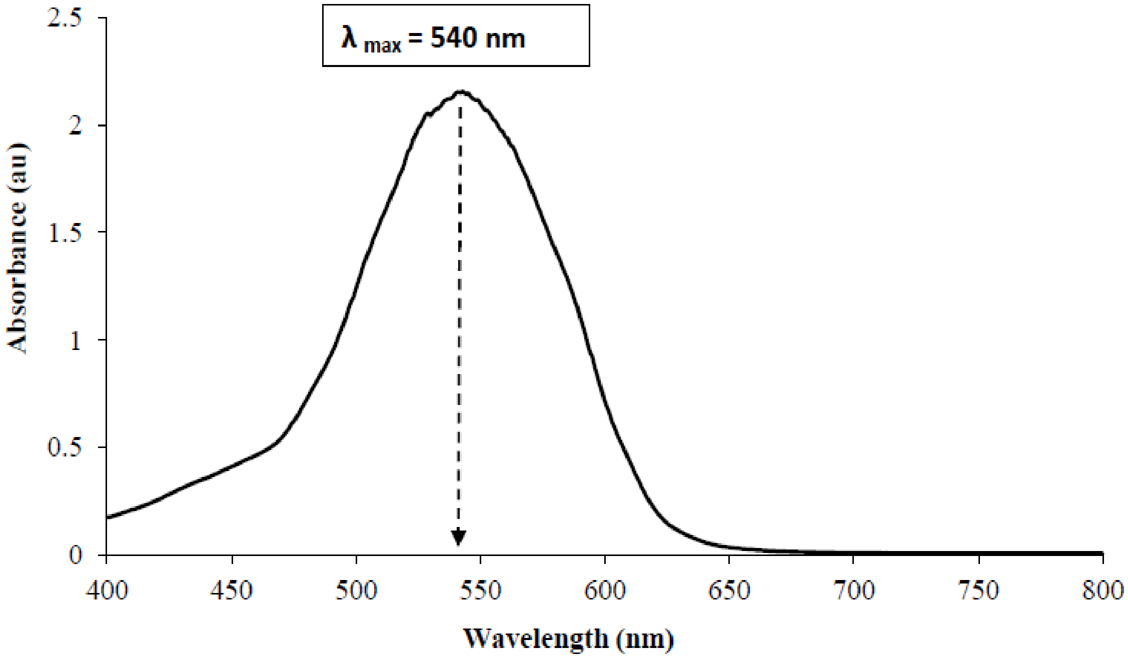


Figure 4.4: Standard Calibration Curve Method for Cr Detection

4.4. Calibration Curve

A calibration curve was developed at λ-max 540 nm using serial dilutions starting from 0.5µg/l to 5 µg/l of a solution as shown in Figure 4.5. The linear calibration curve with the equation absorbance = 0.0867x + 0.0272, where absorbance units are in milliabsorbance·min^{-1} and concentration is measured in ppm (µg/L), gave a correlation coefficient $R^2 \geq 0.9996$.

4.4.1. Analysis of Samples on UV-Visible Spectrometric

A calibration equation (y = 0.0867x + 0.0272, R^2 = 0.9996, where y is absorbance and x is concentration in ppm or µg/l) derived from a calibration curve was plotted from standards (0.5 µg/l, 1 µg/l, 2.5 µg/l, 3.5 µg/l and 5 µg/l) for the quantization of Cr (VI) in synthesized wastewater samples. However, due to the low sensitivity to low Cr (VI) concentrations and low detection limits of Cr (VI) in synthesized samples, light pink color developed with 1,5-diphenylcarbazide. Synthesized samples were spiked with 1 mL, 2 mL, 5 mL, 7 mL and 10 mL of a 5 µg/l Cr (VI) standard. Figure 4.5. show the spiked curves that were used for the quantization of Cr (VI).

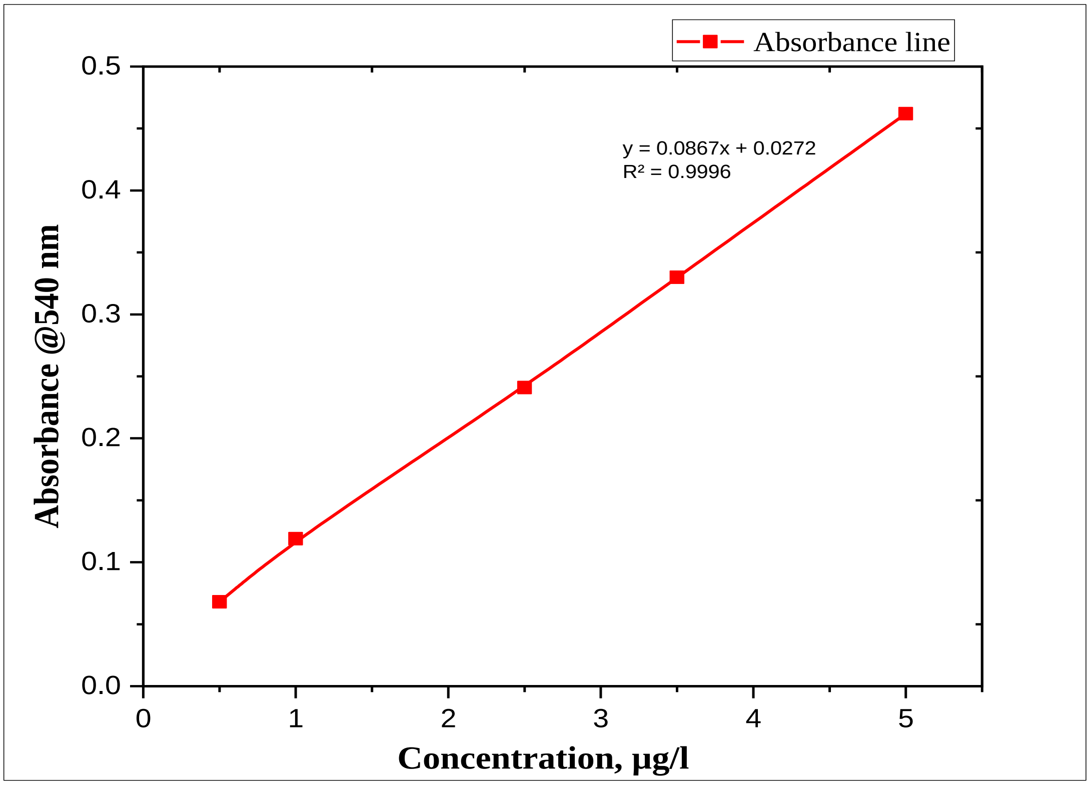


Figure 4.5: Chromium Standard Curve for Synthesized Samples at λ-max 540 nm.

4.5. Optimization of process parameters

The pH values of synthetic wastewater solutions were adjusted to 3.0–7.0 by using 1.0 M HCl and 1.0M NaOH solutions. Effect of Adsorbent dosage was determined and Contact time was optimized for better removal efficiency. UV-Visible spectrophotometer was used to find out the concentration of Cr (VI) in the filtrate solution.

Table 4.3: Study Parameters Used for the Batch Adsorption

Contact Time (min)	30	60	90	120
pH	pH is maintained at levels (3, 4, 5, 6 & 7)			
Adsorbent Dose (mg) Applied at each pH level	10, 20, 30, 40, 50	10, 20, 30, 40, 50	10, 20, 30, 40, 50	10, 20, 30, 40, 50

4.5.1. Effect of Contact Time

The effect of contact time on the removal efficiency of chromium, lead and cadmium ions using synthesized nickel ferrite nanoparticles (NFN's) were studied at room temperature and the obtained results were shown in Figure 4.6.

Table 4.4: Effect of Contact Time on Removal Efficiency

Contact Time (min)	**Avg. Removal Efficiency (%)**		
	Chromium	**Lead**	**Cadmium**
30	79.36	72.73	80.248
60	82.93	73.99	82.27
90	85.21	76.86	84.45
120	84.06	77.41	84.35

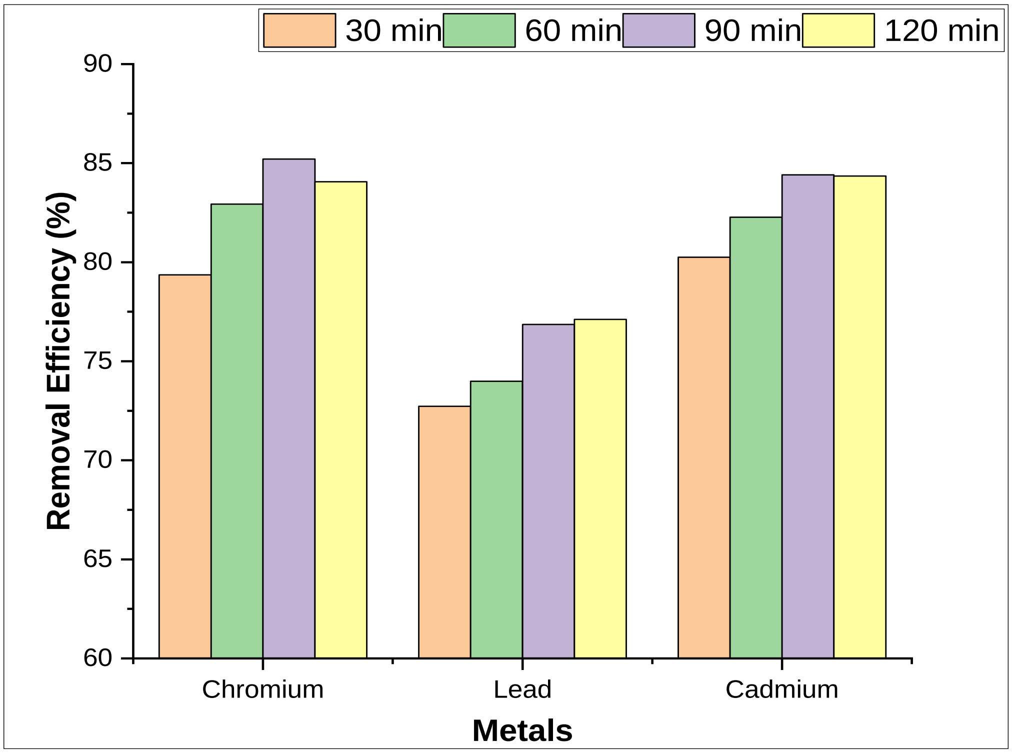


Figure 4.6: Effect of Contact Time on Adsorption of Cr (VI), Pb (II) and Cd (II)

From the obtained result, it was found that the removal of metal ions increases as increase contact time and attained equilibrium level at 90 min, after which further increase in time did not bring any further improvement for the removal of metal ions, but resulted in desorption of metal ions from the adsorbent surface. Nickel ferrite nanoparticles show maximum removal efficiency of 85.21 % for Cr (VI) ions in 90 min, 77.41 % for Pb (II) ions in 120 min and 84.45 % for Cd (II) ions in 90 min applied constant (e.g 10 mg) of adsorbent dosage. The results show that the different metal ions attained equilibrium at different times and the higher removal efficiency is for the removal of Cd (II)and the lower removal efficiency is for the removal of Pb (II).

4.5.2. Effect of pH

The effect of pH was studied from a range of 3 to 7 under the precise conditions (at optimum contact time 30 to 120 min @ 250 rpm shaking speed, with 10 mg of the adsorbent used at room temperature). In all experiments, the NFN's dose (10 mg) was kept constant to the assessed effect of pH on the adsorption of metal ions using NFN's as shown in Figure 4.7.

Table 4.5: Effect of pH on Removal Efficiency

Metals	Avg. Removal Efficiency (%)				
	pH = 3	pH = 4	pH = 5	pH = 6	pH = 7
Chromium	85.8075	85.28	82.39	81.99	81.785
Lead	72.775	72.945	75.2475	72.275	66.905
Cadmium	73.4925	73.505	73.9695	71.7615	68.1165

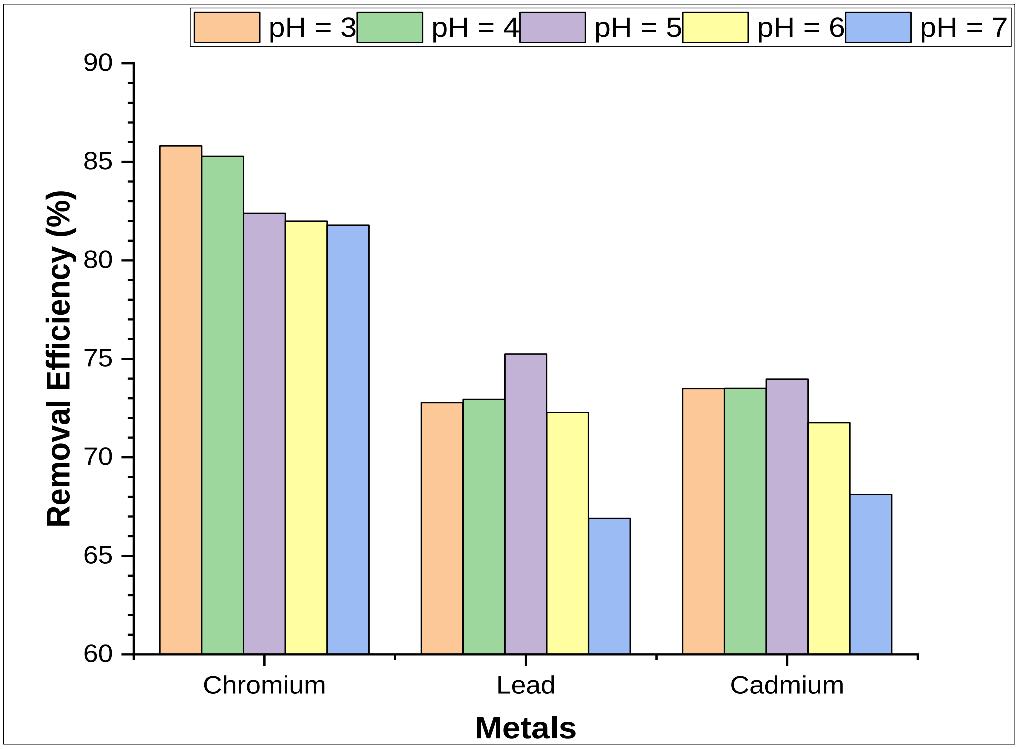


Figure 4.7: Effect of pH on Adsorption of Cr (VI), Pb (II) and Cd (II)

Curves were obtained to assess the effect of pH their interactive effect on the adsorption. It was observed that with an increase in the pH from 3 to 7 of the synthesized wastewaters, the removal efficiencies of Cr (VI) decreased as pH increased and maximum removal efficiency was obtained at pH 3 for nickel ferrite nanoparticles. Hence the removal efficiency of Chromium gradually decreased was found as pH increased. The maximum removal efficiency of Lead and Cadmium was found at pH 5. NFN's shown maximum removal efficiency of 85.8 % for Cr (VI) ions at pH 3, 75.25 % for Pb (II) ions at pH 5, 73.97 % for Cd (II) ions pH 5 on 10 mg of adsorbent dosage. It was noted that as the pH of water decreases, the toxicity of the solution increases, the reason to obtained maximum removal efficiency of metal ions. The removal rate of metal ions increased with low pH values, at low pH values, NP's is justified because of decreasing H+ in the water environment. Many researchers have shown that as pH increases the surface of adsorbent becomes more negatively charged which causes repulsion between metal ions (adsorbed) and NP's (adsorbent). therefore, the removal efficiency decreases with an increase in pH. The surface of NP's became positively charged at low pH values due to protonation and adsorption was enhanced due to electrostatic forces between the nanoparticles and the negatively charged $Cr_2O_7^{-2}$ and $HCrO_4^{-2}$.

4.5.3. Effect of Adsorbent Dosage

Adsorbent dosage was varied from 10 to 50 mg, under the specific condition (contact time of 90 min, 200 rpm, room temperature and pH of 3 - 5) using Nickel ferrite nanoparticles (NFN's). The relationship between adsorbent dosage and removal efficiency of metal ions from synthesized wastewater is shown in Figure 4.8.

Table 4.6: Effect of Adsorbent Dose on Removal Efficiency

Adsorbent Dose (mg)	Avg. Removal Efficiency (%)		
	Chromium	**Lead**	**Cadmium**
10	86.41	77.41	84.45
20	86.95	77.68	84.27
30	89.8	78.66	84.96
40	89.09	79.47	87.24
50	89.2	78.49	87.366

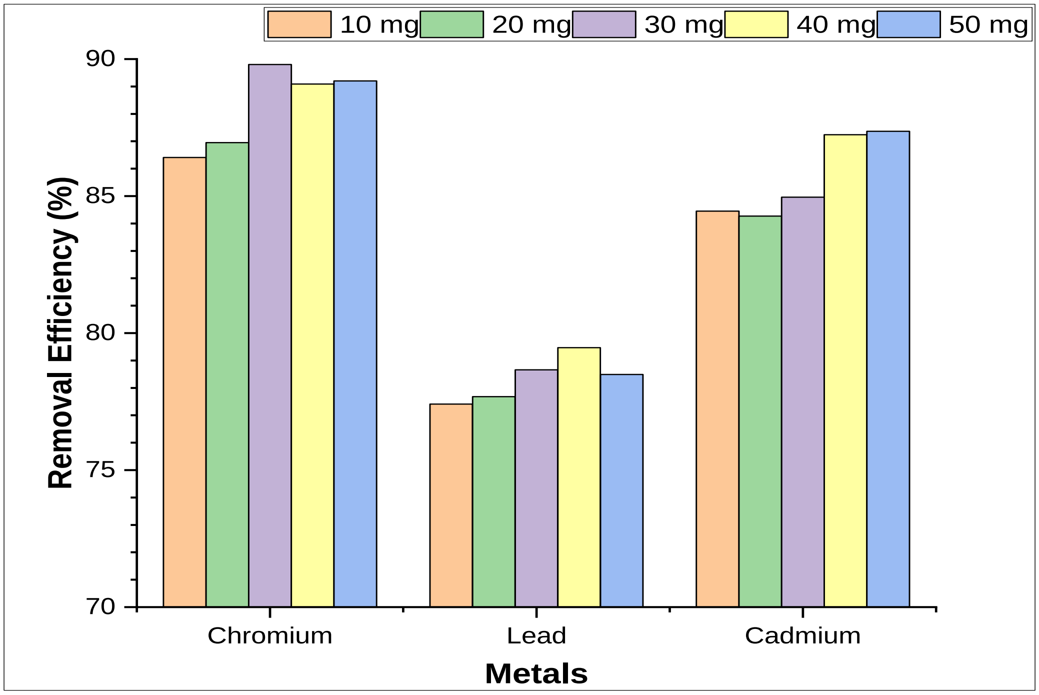


Figure 4.8: Effect of Adsorbent Dose on Adsorption of Cr (VI), Pb (II) and Cd (II)

Nickel ferrite nanoparticles (NFN's) shown maximum removal efficiency of 89.8 % for Cr (VI) ions on 30 mg of adsorbent dosage, 79.47 % for Pb (II) ions on 40 mg and 87.24 % for Cd (II) ions on 40 mg of adsorbent dosage. The results clearly have shown that the increase in adsorbent dosage also increases the removal efficiency of metal ions and maximum removal efficiency was attained at a particular adsorbent dosage, until an optimal dosage of 30 mg or Cr (VI), 40 mg for Pb (II) and Cd (II) was reached after which the removal was more or less the same. Starting from 10 mg with an increment of 10 mg, the dosage was increased up to 50 mg showing increase removal with increased dosage until the maximum removal is achieved at 30 mg which is the optimum dosage for removal of Cr (VI), 40 mg for Pb (II) and Cd (II). Increasing the percentage of adsorption with adsorbent dose may be due to the increase in adsorbent surface area and the availability of more adsorption sites. The rate of adsorption, however, decreased with an increase in adsorbent dose after the optimal value. This is maybe due to the overlapping of adsorption sites as a result of overcrowding of adsorbent particles. When the NFN's were dispersed into synthesized wastewater with a high dose of NFN's it resulted in decrease adsorption which was the major cause of reduction of the contact surface of nanoparticles for the removal of metal ions.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this study, NFN's were synthesized by co-precipitation method and were characterized by XRD, SEM and EDS. Results showed that the NFNs were spherical, homogeneous and discrete particles shape.

1. Adsorption through NFN's of size 60 – 80 nm using the co-precipitation method can be considered as a simple and efficient method for the removal of heavy metal ions from wastewater.
2. Max. removal efficiency 89.8% for Cr at pH 3, Pb and Cd were 79.4% and 87.3% at pH 5 respectively under optimal conditions (contact time of 90 min, agitation speed – 250 rpm, room temperature and pH of 3 - 5).
3. It is found that the pH value was inversely proportional to the adsorption capacity of Cr while the adsorption efficiency of Cd and Pb increases as pH increases from pH 3-5.

5.2. Recommendations

Following are some of the suggestions for carrying forward the work reported in this thesis:3

1. Adsorption through NFN’s could be explored for removal of other heavy metals i.e. As+, Zn+, Ni+, Co+, Cu+ & Hg+ and organics i.e. COD and BOD
2. Other methods can be used for the preparation of NFN’s over co-precipitation to obtain a more uniform size & structure of particles.

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