# SYNTHESIS AND CHARACTERIZATION OF NICKEL AND COBALT OXIDE NANOPARTICLES

*Project work by*

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## MAHATMA GANDHI UNIVERSITY

*In partial fulfillment of the requirements for the award of degree of*

**MASTER OF SCIENCE IN**

**PHARMACEUTICAL CHEMISTRY**

*Under the Guidance Of*
**Dr. Mary Joseph**

DEPARTMENT OF CHEMISTRY

BHARATA MATA COLLEGE, THRIKKAKARA

DEPARTMENT OF CHEMISTRY

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# CERTIFICATE

This is to certify that the project report entitled **"SYNTHESIS AND CHARACTERISATION OF NICKEL AND COBALT OXIDE NANOPARTICLES "** is an authentic record of the project work carried out by Ms. RAJALAKSHMI K R (Reg.no:180011017734) in partial fulfillment of the award of the degree of Master of Science in Pharmaceutical chemistry at Bharata Mata College, Thrikkakara affiliated to Mahatma Gandhi University, Kottayam under my guidance and supervision during 2018-2020.

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# DECLARATION

I, Rajalakshmi K R, hereby declare that the project report entitled **"SYNTHESIS AND CHARACTERIZATION OF NICKEL AND COBALT OXIDE NANOPARTICLES''** is a bona-fide record of the work carried out by me under the guidance of **Dr. Mary Joseph**, Associate Professor Department of Chemistry, Bharata Mata College Thrikkakara during my M.Sc. Degree in Pharmaceutical Chemistry.

**Thrikkakara**

**17/07/ 2020** **RAJALAKSHMI K R**

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**RAJALAKSHMI K R**

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# CHAPTER I

# INTRODUCTION AND REVIEW OF LITERATURE

## 1.1 Introduction

A nanoparticle is a microscopic particle with a dimension less than 100nm. Nanoparticle research is currently an area of intense scientific research, due to a wide variety of potential applications in biomedical, optical and electronic fields. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures

Nano materials are of interest due to the optical, electrical, magnetic and mechanical properties. Some nano materials are occur naturally but of particular interest some are engineered. The application of nano materials extended for the use in information technology, bio engineering and environmental applications. They used in medicines for the purpose of diagnosis, imaging and drug delivery.

Synthesized nano materials are designed to take the advantage of their small size and novel properties which are generally not seen in their bulk counterparts. Nano materials have increased surface area to volume ratio. The quantum effects have importance in the material properties and characteristics leading to novel properties.

# 1.2 Classification of Nano materials

Nano materials can be classified based on three:

- Materials
- Dimension
- Origin

## 1.2.1 Based on materials

### 1.2.1.1 Carbon based NMs

They contain carbons and found in structures such as hollow tubes or spheres. Fullerens ($C_{60}$), Carbon Nano Tubes (CNTs), graphene and carbon nano fibers are included in this category. Arc discharge and chemical vapour deposition are the important methods for carbon based nano materials synthesis.

### 1.2.1.2 Inorganic based NMs

These include metal and metal oxide NMs. Au, Ag NMs are examples for metals and $TiO_2$ and ZnO.

### 1.2.1.3 Organic based NMs

These include NMs produced from organic matter excluding carbon based and inorganic based NMs. Micelles, dendrites and liposome NPs belongs to this category.

### 1.2.1.4 Composite based NMs

In this category NPs combine with other NPs or bulk materials. The composites may be any combinations of carbon based, organic or inorganic based with bulk materials.

## 1.2.2 Based on dimensions

Based on dimension NMs are classified as 0D, 1D, 2D and 3D NMs. This classification is based on the electron movement along the dimensions in the NMs. In 0D NMs, electros are entrapped in dimensionless space whereas in 1D, 2D and 3D NMs, electrons move along x axis, x-y axis and x-y-z axis respectively.

0D NMs – Nano rods, nanoparticles
1D NMs – Nanowires and nanotubes
2D NMs – Very thin surface coatings
3D NMs – Crystals

## 1.2.3 Based on origin

This category includes natural and synthetic NMs.

### 1.2.3.1 Natural NMs

These NMs are produced in nature by biological species. They produced throughout the earth's sphere.

### 1.2.3.2 Synthetic NMs

NMs are produced by physical, chemical and biological methods. The major challenge is whether the existing knowledge is enough to forecast their behavior or if they exhibit distinct behavior different from natural NMs.

## 1.3 Properties of Nano materials

Nano materials have the structural features between atoms and the bulk materials. Due to their small dimensions, they have greater surface area to volume ratio. The nanometer size of NMs have spatial confinement effect on the materials, which give quantum effect.

The energy barriers and charge carrier density in the materials can be modified quite different from their bulk and thus will modify the electronic and optical properties. The enhanced chemical stability leads to the better mechanical properties of the bulk materials.

### 1.3.1 Optical properties

One of the most useful aspects of NMs is their optical properties. Applications based on this properties includes lasers, optical detectors, solar cells, photo catalyst, sensors and biomedicines.

Optical properties depends on size, shape, doping and interaction with surrounding environment. When an anisotropy is added to the nanoparticles, like growth of nano rods, the optical properties of the NPs change dramatically.

### 1.3.2 Electrical properties

Electrical properties of NPs explain the electrical conductivity and photo conductivity of nano tubes and nano rods. With decreasing diameter of the wire,

the number of electron wave modes contributing to electrical conductivity is becoming increasingly smaller by well-defined quantized steps. In electrically conducting CNTs, only one electron mode is observed, which give the electric current.

### 1.3.3 Magnetic properties

It is possible that non-ferromagnetic bulk materials can exhibit ferromagnetic like behavior when prepared in nano size. The magnetic NPs of metals like Au can be can be prepared from non-magnetic bulk material. It became possible if the gold NPs are capped with appropriate molecules. Permanent magnetism was observed up to room temperature for thiol capped gold NPs.

## 1.4 Synthesis of Nano materials

NMs can be prepared by chemical and physical methods.

### 1.4.1 Chemical synthesis methods

The possibility of controlling particle size even at nanometer scale is an advantage of chemical synthesis.

### 1.4.1.1 Chemical reduction

It is a most common method for synthesis of organic and inorganic NPs. This method results in the agglomeration forming colloidal NPs. Usage of capping agents such as poly vinyl alcohol helps to stabilize the particles from sedimentation and agglomeration.

### 1.4.1.2 Sol-gel method

By this method NPs can be prepared in desired shapes. First, sol formation is carried out by dissolving metal alkoxide, metal-organic or inorganic precursors in a suitable solvent. Then the sol is dried, a polymeric network is formed in which the solvent molecules are trapped inside a gel. Subsequent drying of the gel followed by calcination sintering give ceramic products.

### 1.4.1.3 Polymerization

In this method the formation of micro emulsion is a very important factor. agriculture, food, metal cutting, enzymatic catalysis etc.

### 1.4.1.4 Microwave-assisted synthesis

It is a better technique over other conventional methods for the synthesis of NPs with smaller sizes and high degree of crystallization. The advantages of this method includes shorter reaction time, reduced energy consumption and a better product yield. It also prevents the agglomeration of the particles formed.

### 1.4.1.5 Sono chemical processing

Implementation of high intensity ultra sound waves as a energy source in respective sol material results in collapse of the bubbles of the sol. The extreme

conditions enables the reactants to cross the activation energy barrier in a very short time to form the products.

#### 1.4.1.6 UV-Initiated photo reduction

In this method the NPs are synthesized in presence of protective and stabilizing agents such as citrate poly vinyl pyrrolidone, at room temperature.

Synthesis and growth of nano rods depends n concentration of poly vinyl alcohol and silver nitrate.

### 1.4.2 Physical synthesis methods

The advantages over chemical method is devoid of solvents and uniform distribution of NPs.

#### 1.4.2.1 Evaporation – Condensation

In this method evaporate metals and alloys using gas and allow to react each other. Then it is condensed using cool gases results in the formation of NPs.

#### 1.4.2.2 Arc discharge/ plasma

This method widely used for the synthesis of fullerens. Direct current arc method is covert inert gases in to ionized with the generation of high temperature and melts the material. The condensation of evaporated materials leads to the formation of NPs.

#### 1.4.2.3 Laser/ Electron Beam Heating

Main principle of this method is to emit electron from electron gun with high temperature and irradiate the material for developing NMs such as CNTs and carbon nanoparticles.

## 1.5 Applications of Nanomaterials

Ability of materials to dramatically change their property at nanoscale has opened up the possibility of marketing new devices, instruments and consumer goods to function in much better ways than was possible earlier. Rapid progress in synthesis and understanding of Nanomaterials in just a few years had led them to enter the world market in a big way.

### 1.5.1 Electronics

Single electron transistor (SET), spin valves, and magnetic tunnel junction are conceptually new devices based on nanotechnology. Such devices are fast, compact, relatively cheap and are finding their way to market. Spin valve devices are already being used in personal computers to read disc which have enabled to increase data storage capacity of hard disc. The flat panel television or computer monitors are products of nanotechnology. Even the coatings used for screens of TV or monitors can be of nanoparticles, which have better properties in terms of color quality and resolution than micro particle coatings.

### 1.5.2 Energy

Nanotechnology will play an important role in the field of energy. We will know that natural energy resources are limited and depleting very fast. The future generations will have to look for alternative sustainable energy sources. There is a considerable amount of research going on to tap hydrogen fuel by splitting water using sunlight in presence of nanomaterials. Material like carbon nanotubes is a special class of Nanomaterials being investigated for its potential

use as hydrogen storage material. There are also attempts going on to increase the efficiency of solar cells for energy production using nanoparticles.

## 1.5.3Automobiles

Even a simple car is made up of a large number of parts and materials. Body structure should be strong, non-deformable or rigid, desirable shape and size. Nanotube composites have mechanical strength better than even steel. Attempts are made to make composites that can replace steel. Nanoparticle paints provide smooth, thin, attractive coating. Some research is going on to explore the possibility of applying a small voltage to change the color of the cars as desired. Very powerful motors known as shape memory alloys are made

using nanoparticles of material like Ni-Ti. They perform better and less power hungry than other motors. Such motors are finding their way in automobiles.

## 1.5.4 Textiles

Textile industry is also quite excited about nanomaterials. Special threads and dyes used in this industry are products of nanotechnology. Some companies are using even silver nanoparticle in washing machines which clothes germ free. Use of silver nanoparticles assures germ-free environment necessary for bandages, surgical purposes and child-care items.

## 1.5.5 Cosmetics

Nanoparticles are also important in cosmetics. Zinc oxide and Titanium oxide nanoparticles of fairly uniform size are able to absorb UV light and protect the skin. Some creams using nanoparticles are already marketed. Nano-based dyes and color are quite harmless to skin and can be used in hair creams and gels.

### 1.5.6 Biotechnology and Medical field

Initial tests of various drug delivery systems, cancer or tumor therapies or detection have been successful using nanotechnology. Nanoparticles being very small are easy to inject and target towards specific portion in a body. Image certain parts of body like in dentistry, bone etc., Nano phosphors are being used. Semiconducting nanoparticles or quantum dots are highly florescent materials and can be used.

## 1.6 Applications of Cobalt oxide Nanoparticles

### 1.6.1 Lithium-ion battery

The anodes of Li-ion battery are made up of Cobalt oxide NPs, because it offers high surface to volume ratio and short path length for Li cation transport, results in high reversible capacity and good cycle life. Cobalt oxide NPs may be anchored on graphene to improve the dimensional stability of the anode.

### 1.6.2 Gas Sensor

Cobalt oxide hollow nanospheres are used in gas sensor electrodes, for the detection of toluene and acetone. Cobalt oxide NPs anchored in CNTs are used for sensing hydrogen and nitrogen oxides.

### 1.6.3 Medicine

Cobalt oxide NPs have been observed to readily enter cells, this property helps in the application in gene therapy and drug delivery. Since Cobalt oxide NPs posses magnetic properties they used as MRI agents.

# 1.7 Characterization of Nanoparticle

Nanoparticles dispersed in the form of colloids in solutions, particles or thin film are characterized by various technique like X-Ray Diffraction (XRD), Transmission Electron Microscope (SEM), Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM), IR and UV-Visible spectroscopic methods. Although these techniques to be used would depend upon the type of material and information one needs to know like size, crystalline type, composition, chemical state, optical and magnetic properties etc.

## 1.7.1 Scanning Electron Microscope (SEM)

SEM uses backscattered electrons from a sample for imaging. Typically, electrons are accelerated up to 30Kev and resolution up to 3-5 nm can be achieved. A cold cathode emits electrons under the application of a very high electric filed. It is also known as filed emitter such SEMs are known as FESEM and are able to give better images than hot filament SEM. The electron beam can be focused to a very small spot size using electrostatic lenses. The fine beam is scanned on the sample surface using a scan generator and backscattered electrons are collected by an appropriate detector. Signal from scan generator along with amplified signal from the electron collector generates image of the sample surface.

When an electron beam is interacting with matter, several processes occur. Inelastic scattering occurs as the beam interacts with the sample and electronic excitation of the constituent atoms occurs. These excitations can lead to valence and core electron excitation and emission. The core hole thus created may get filled by an electron de-excitation resulting in X-rays. The de-excitation can also result in electron ejection called auger emission. In addition, collision of the primary beam can also lead to excitation of lattice vibration. All these electrons can be used to gather microscopic information of the sample. In addition, they can also be used to obtain chemical or compositional information

as in the case of auger electrons or structural information as in the case of back scattered electrons.

## 1.7.2 Transmission Electron Microscope (TEM)

The TEM uses a high voltage electron beam to create an image. The electrons are emitted by an electron gun commonly fitted with a tungsten filament as the electron source. The electron beam is accelerated by an anode typically at 100KeV with respect to cathode; focused by electrostatic and electromagnetic lenses and transmitted through the specimen that is in part transparent to electron in part scatters them out of the beam. When it emerges from the specimen, the electron beam carries information about structure of the specimen that is magnified by the objective lens system of the microscope. The special variation in this information is vied by projecting the magnified image in to a fluorescent viewing screen coated with phosphor or scintillated material such as zinc sulfide. The image can be photographically recorded by exposing a photographic film or plate directly to the electron beam, or a high resolution phosphor may be coupled by means of a lens optical system or CCD camera. The image detected by the CCD may be displayed on a monitor or computer.

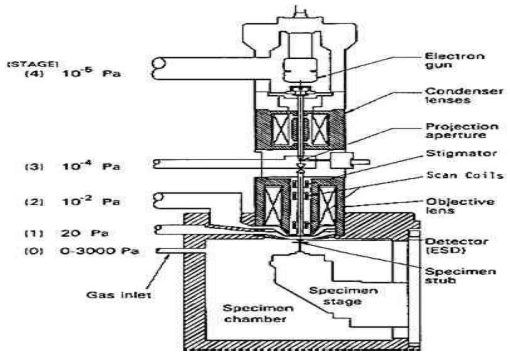



Figure 1. Transmission Electron Microscopy

## 1.7.3 X-ray Diffraction (XRD)

X-ray crystallography is a method of determining the arrangement of atoms with in a crystal, in which a beam of X-ray strikes a crystal and diffracts in too many specific directions. From the angles and intensities of the diffracted beam a crystallographer can be produce a three-dimensional picture

of the density of electron with in crystal. Analysis of these diffraction patters allows obtain information such as lattice parameter, crystal structure, sample orientation, and particle size. We will only mention that lattice parameters are obtained from the Bragg formula: $2d \sin\theta = n\lambda$

The intensity of the diffracted X-ray is measured as a function of a diffraction angle $2\theta$. The intensities of the spot provide information about the atomic basis. The sharpness and shape of the spot are related to the perfection of the crystal. The two basis procedure involves either a single crystal or a powder. With single crystal, a lot of information about the structures can be obtained.

## 1.7.4 UV-Visible spectroscopy

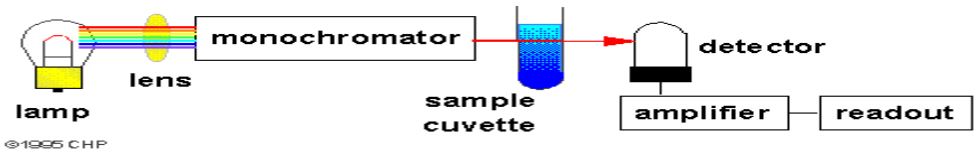



Figure 2. UV-Visible spectrophotometer

UV-Visible spectroscopies are most often liquids, although the absorbance of gases and even of solids can be measured. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape, commonly with an internal width of 1 cm. the type of

sample container used must allow radiation to pass over the spectral region of interest. The most widely applicable cuvettes are made of high-quality fuse silica or quarts glass because these are transparent through the UV visible and near IR regions. Using this technique, we can find d absorbance (a), path length (b), concentration(c), by using Beer-Lambert's law

$$A = \log(I/I_0) = abc$$

Where, a=molar absorption coefficient,

b=path length,

c=concentration

## 1.7.5 FTIR spectroscopy

In Fourier transform spectroscopy allowing only one wavelength at a time to pass through the detector, this technique lets through a beam containing many different wavelengths of light at once, and measures the total beam intensity. Next, the beam is modified to contain a different combination of wavelengths, giving a second data point. This process is repeated many times. Afterwards a computer takes all this data and works backward to infer how much light there is at each wavelength. To be more specific, between the light source and the detector, there is a certain configuration of mirrors that allows some wavelengths to pass through but blocks others. The beam is modified for each new data point by moving one of the mirrors; this changes the set of wavelengths that can pass through.

As mentioned, computer processing is required to turn the raw data (light intensity for each mirror position) into the desired result (light intensity for each wavelength). The raw data is sometimes called an "interferogram". Because of the existing computer equipment requirements and the ability of light to analyze very small amounts of substance, it is often beneficial to automate many aspects of the sample preparation.

# 1.8 AIM AND OBJECTIVES

## Aim

To synthesis Ni and $Co_3O_4$ nanoparticles by the method on the reported work by Ayesha Khan etal [4], and also to modify the method using Aloe Vera extract for the synthesis of $Co_3O_4$ nanoparticles. The proposed work also aims to characterize the synthesized nanoparticles.

## Objectives

Since Ni and $Co_3O_4$ nanoparticles have medicinal applications, this project aims to synthesize Ni and $Co_3O_4$ nanoparticles through a chemical reduction method adopted for the synthesis of Copper nanoparticles in the literature[4]. The method was also modified by using Aloe vera extract as an antioxidant and capping agent for the synthesis of Cobalt oxide nanoparticles. The characterization of synthesized Nickel and Cobalt oxide nanoparticles was done using UV-Visible spectroscopy and X-Ray Diffraction (XRD) studies.

# Chapter II

# MATERIALS AND METHODS

## 2.1 Materials and Methods

All of the chemicals used in the work were analytical grade and were commercially obtained.

The chemicals used for the synthesis of Nickel nano particles are Nickel (II) sulfate hexahydrate salt, $NiSO_4.6H_2O$, of 98% purity (Merck) Starch $(C_6H_{10}O_5)_n$ (1.2%) Ascorbic acid (Nice 99 %) and Sodium hydroxide NaOH (Merck).

For the synthesis of CoO nano particles, Cobalt nitrate hexahydrate salt, $Co(NO_3)_2.6H_2O$), of 98% purity (Merck), was used.

In an alternative method of synthesis of CoO nano particles Aloe Vera extract was used in place of Starch and ascorbic acid.

## 2.2 Synthesis of Nickel nanoparticles

### Chemical Reduction method

The copper nanoparticles were synthesized by chemical reduction process using Nickel (II) sulphate hexahydrate $NiSO_4.6H_2O$ as precursor salt. Starch $(C_6H_{10}O_5)_n$ (1.2%) is used as the capping agent. Ascorbic acid was used as the antioxidant. Sodium hydroxide NaOH was used to adjust the pH and accelerate the reduction reaction in water.

The preparation method starts with addition of 100ml 0.1M Nickel (II) sulphate hexahydrate solution into 120 mL of starch (1.2%) solution with vigorous stirring for 30 min to obtain a blue solution (a). In the second step, 50mL of 0.2M ascorbic acid is added to the reaction mixture under continuous rapid stirring. Subsequently, 30mL of 1M sodium hydroxide solution was slowly added to the solution with constant stirring until precipitation.The appearance of the colour change indicates that the reduction reaction had been started. The Mixture is heated to about 2 hours at 80$^{o}$C, the colour of the solution turned olive green (c). After the completion of reaction, the solution was taken from the heating mantle and allowed to settle overnight and the supernatant solution was then discarded cautiously. A very dilute solution of the reaction mixture is observed in a UV chamber for fluorescence. The precipitates were separated from the solution by centrifugation and washed with distilled water and alcohol for 3 times to take out the excessive starch bound with the nanoparticles. Olive green color precipitate obtained is dried in an oven. After drying, nanoparticles were stored in glass vial for further analysis.

Fig: a. $NiSO_4$ +starch solution

Fig: b. $NiSO_4$ +starch +Ascorbic aid

Fig: c. $NiSO_4$ +starch +Ascorbic acid +NaOH

## 2.3 Synthesis of Cobalt oxide nanoparticles

### (a) Chemical Reduction Method

The Cobalt nanoparticles were synthesized by chemical reduction process using Cobalt(II) nitrate hexahydrate $Co(NO_3)_2.6H_2O$ as a precursor salt and starch as capping agent. 50mL of 0.2M ascorbic acid was used as the antioxidant and 30mL of 1M sodium hydroxide solution was used to adjust the pH of the reaction mixture and accelerate the reduction reaction in water.

The preparation starts with addition of 100ml 0.1M Cobalt nitrate hexahydrate solution into 120 mL of starch (1.2%) solution with vigorous stirring for 30 min (a). In the second step, 50mL of 0.2M ascorbic acid is added to the reaction mixture under continuous rapid stirring. Subsequently, 30mL of 1M sodium hydroxide solution was slowly added to the reaction mixture with constant stirring to obtain a purple coloured solution (b). The appearance of this colour change, to purple indicates that the reduction reaction had been started. The mixture is heated to about 2 hours at $80^oC$, the colour of the solution turned black (c). After the completion of reaction, the solution was taken from the heating mantle and allowed to settle overnight and the supernatant solution was then discarded cautiously. A very dilute solution of the reaction mixture is observed in a UV chamber for fluorescence.

The precipitates were separated from the solution by centrifugation and washed with hot water for 3 times to take out the excessive starch bound with the nanoparticles. The black precipitate obtained is dried in an oven. After drying, nanoparticles were stored in glass vial for further analysis.

Fig: a. $Co(NO_3)_2$ +starch solution

Fig: b. $Co(NO_3)_2$ +starch +Ascorbic aid

Fig: c. $Co(NO_3)_2$ +starch +Ascorbic acid +NaOH

## (b) Synthesis of $Co_3O_4$ NPS by replacing starch and ascorbic acid by Aloe Vera extract

*Extraction of Aloe Vera leaf extract:*

The fresh Aloe Vera leaves were collected and thoroughly washed. It is then peeled and the gel is collected. It is then homogenized with adequate quantity of water in a mixer grinder and then filtered to remove the ungrounded gels particles to obtain a homogeneous mixture. The filtrate was stored in a refrigerator for the work.

### *Synthesis*

The Co nanoparticles were synthesized by using Cobalt nitrate hexahydrate as precursor salt and aloe vera extract. Aloe Vera extract was acting as a capping agent as well as an anti-oxidant. 30mL of 1M sodium hydroxide solution was used to adjust the pH of the reaction mixture and accelerate the reduction reaction in water

The preparation starts with addition of 100ml 0.1M Cobalt nitrate hexahydrate solution into 120 mL of aloe vera extract solution

with vigorous stirring for 30 minutes (a). Subsequently, 30mL of 1M sodium hydroxide solution was slowly added to the prepared solution with constant stirring to obtain a dark green coloured solution (b). The appearance of this colour change to dark green indicate that the reduction reaction had been started. The Mixture is heated to about 2 hours at 80$^{o}$C, the colour of the solution turned black (c). After the completion of reaction, the solution was taken from the heating mantle and allowed to settle overnight and the supernatant solution was then discarded cautiously. A very dilute solution of the reaction mixture is observed in a UV chamber for fluorescence. The precipitates were separated from the solution by filtration and washed with distilled water and alcohol for 3 times to take out the excessive aloe vera gel particles bound with the nanoparticles. Black precipitate obtained is dried in an oven. After drying, nanoparticles were stored in glass vial for further analysis.

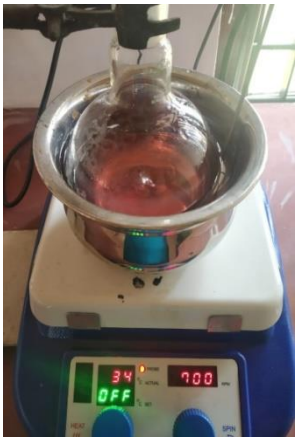


Fig: a. $Co(NO_3)_2$ + Aloe Vera extract

Fig: b. $Co(NO_3)_2$ + Aloe Vera extract + Ascorbic

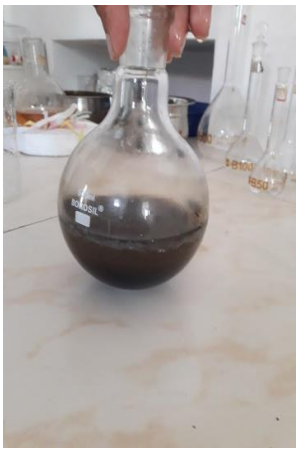


Fig: c. $Co(NO_3)_2$ + Aloe Vera extract + Ascorbic acid + NaOH

## 2.4 Characterization of nanoparticles

Several characterization techniques are available to study solid surfaces of Nano particles but a single characterization method alone can be used to explain their structures.

In this study synthesized samples were studied by use of UV–Visible absorption spectroscopy from a double beam spectrophotometer in the wavelength range from 190 to 1100 nm and X-ray Diffraction (XRD) studies were also carried out to find the particle size.

# Chapter III

# RESULTS AND DISCUSSIONS

In the preliminary studies Nickel and Cobalt oxide nano particles were synthesized by the chemical reduction method.[16] In this reduction processes ascorbic acid provide the right conditions for rapid reduction and subsequent nanoparticle formation. Capping agents like starch is used in nanoparticle synthesis to inhibit nanoparticle overgrowth and aggregation as well as to control the structural characteristics of the nanoparticles formed during the reduction process in a precise manner.

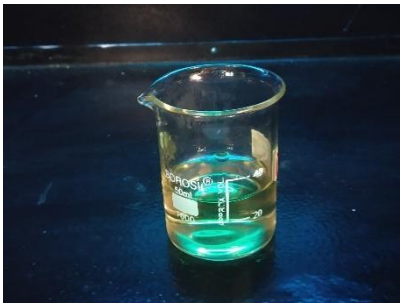
In the second phase of the work the starch and ascorbic acid which are acting as the antioxidant and capping agent respectively are successfully replaced by Aloe vera extract. The green color and black color characteristic of well-defined Nickel and Cobalt metal nanoparticles respectively is essentially obtained after 2 hrs of heating around $80^0$C and is much darker at other times. It also appears that these particles have stability under ambient atmosphere. The mechanism responsible for the change in color remains unclear: it may be due to reduction, re dissolution of the particles, or both at the same time.

## 3.1 Identification of Nano particle formation.

Fluorescence from metal nanoparticles, falls in the visible region due to sp–d band transition of electrons, the fluorescence gets enhanced due to interaction with localized surface plasmon.[17]. The fluorescence obtained in the reaction mixtures are clear indication of nanoparticle formation.

a) Chemically reduced Ni Nanoparticles

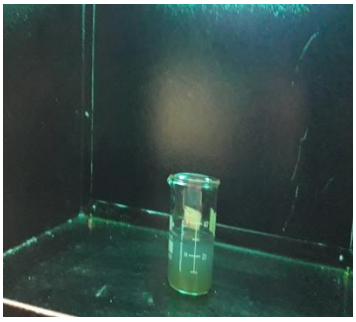
**In the absence of UV**



**In the presence of UV**

b) Chemically reduced $Co_3O_4$ nanoparticles

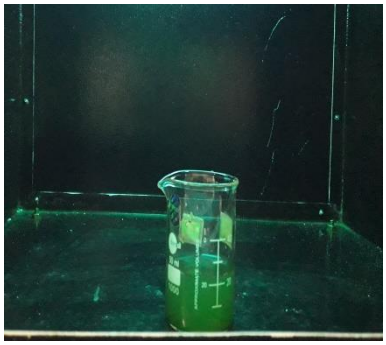
**In the absence of UV light**



**In the presence of UV light**

c) $Co_3O_4$ NPS obtained by replacing starch and ascorbic acid

**In the absence of UV light**



**In the presence of UV light**

## 3.2 Characterization of nanoparticles

### 3.2.1 UV – Visible spectrum of Cobalt oxide nanoparticles

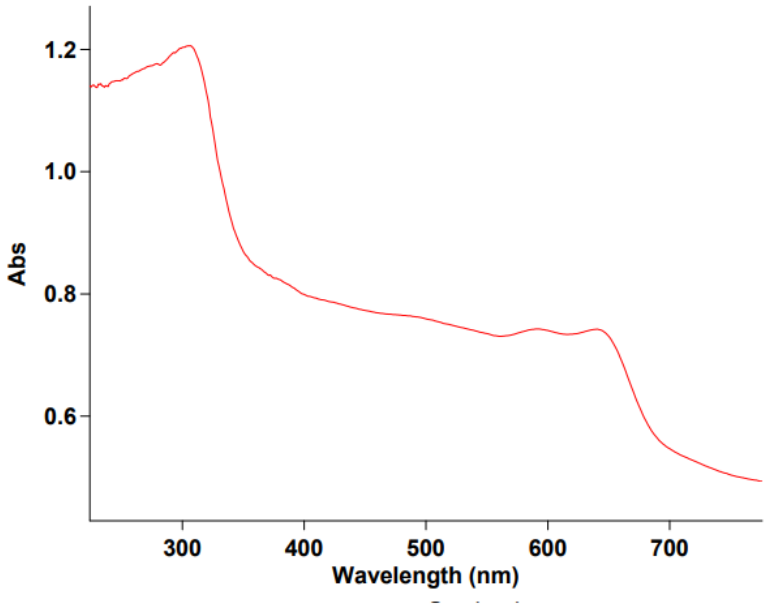



**Fig a: UV-Visible spectrum of $Co_3O4$ NPs by reduction method**

The Cobalt oxide nanoparticles by reduction method show peak at 305nm due to excitation of surface plasmon vibrations.

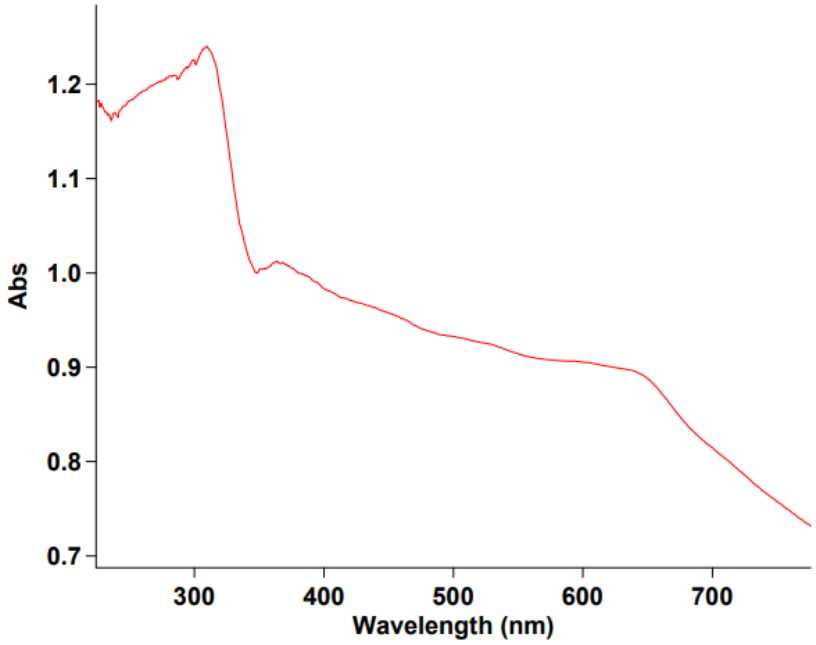



**Fig b: UV-Visible spectrum of $Co_3O_4$ by replacing starch and ascorbic acid**

The Cobalt oxide NPs by replacing starch and ascorbic acid show peak at 310nm due to excitation of surface Plasmon vibrations.

Small metal nanoparticles exhibit the absorption of UV- visible electromagnetic region by the collective oscillation of conduction electrons at the surface. This is known as the surface Plasmon resonance effect. The interest in this effect is the possibility of using it as a tracer for the presence of metal nanoparticles with a simple UV-visible spectrometer.

The size dependence of the plasmon resonance for particles smaller than 20 nm is a complex phenomenon. One interesting feature is the increase in the bandwidth of the resonance with the decrease in the size of the particles due to electron scattering enhancement at the surface. The shift in the resonance and the variation in its bandwidth are thus interesting parameters to characterize the metal nanoparticles

## 3.2.2 X-ray Diffraction Pattern of Nickel nanoparticles

X - ray crystallography was used as a method of determining the arrangement of atoms within a crystal and also the size of the copper nanoparticle from Debye Scherer equation. The result of the x-ray diffraction (XRD) analysis of sample are plotted in Figure below

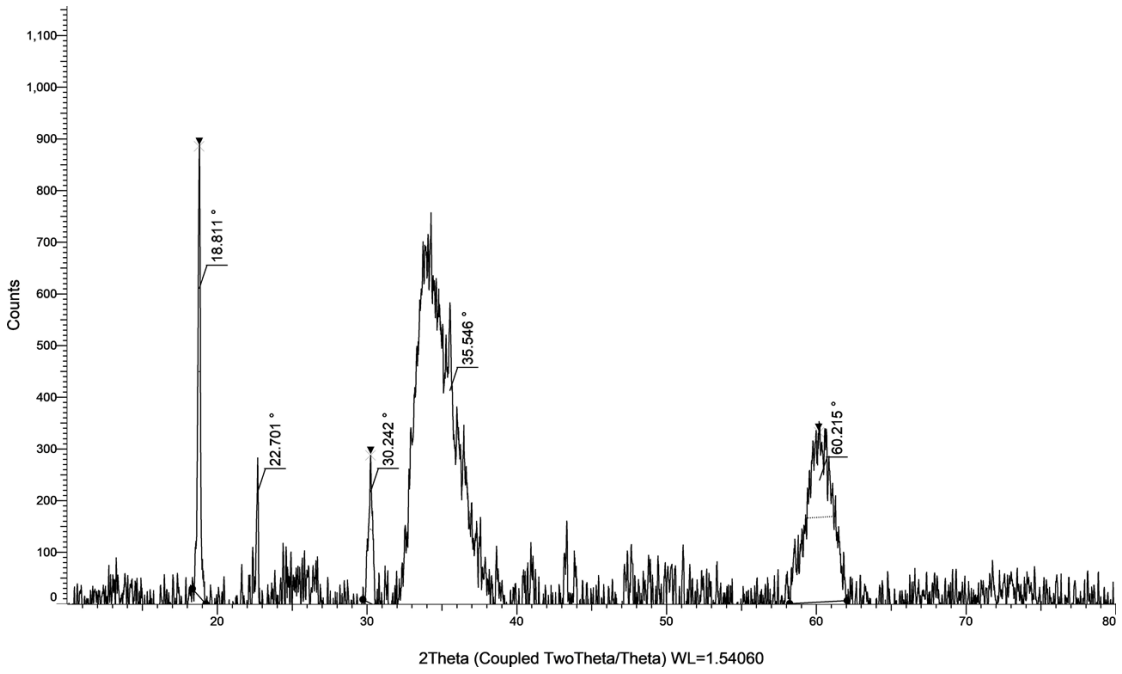



**Fig c: XRD of Ni NPs**

The mean size of nanocrystals was measured from the broadening of the diffraction peaks corresponding to the most intensive reflections. Scherrer equation was used to determine the crystallite size from XRD diffraction pattern measured for nanoparticles:

$$D=k\,\Lambda/\,\beta\,\cos\Theta$$

Where K is the Scherrer constant (0.9), $\beta$is full width at half maximum (FWHM) which can be obtained from the XRD pattern, $\Theta$ is the diffraction

angle, d is the averaged dimension of crystallites in nanometers and $\Lambda$is the wavelength of X-ray used which can be obtained from Bragg's equation, $n\Lambda=2d\sin\Theta$, where n=1; $\Theta$ and d can be obtained from XRD pattern.

$2\Theta$value corresponding to the high intensity peak is $18.811^{\circ}$. From this the value of $\Theta$ can be determined and is found to be $9.4055^{\circ}$, $\Lambda$=1.5406nm, $\beta$=0.179.

Therefore,

$$D = \frac{0.9x1.5406x180}{0.179\times\cos(9.4055)\times3.14\times10} = 45.01nm$$

The size of the Nickel nanoparticle calculated from the above spectrum using the Scherrer equation is equal to 45.01nm.

### 3.2.3 X-ray Diffraction Pattern of Cobalt oxide nanoparticles

X - ray crystallography was used as a method of determining the arrangement of atoms within a crystal and also the size of the Cobalt nanoparticle from Debye Scherrer equation. The result of the x-ray diffraction (XRD) analysis of 2 samples of Cobalt nanoparticles infinity are plotted in the figure below.

The mean size of nanocrystals was measured from the broadening of the diffraction peaks corresponding to the most intensive reflections. Scherrer equation was used to determine the crystallite size from XRD diffraction pattern measured for nanoparticles:

$$D=k\,\Lambda/\,\beta\cos\Theta$$

Where K is the Scherrer constant (0.9), $\beta$is full width at half maximum (FWHM) which can be obtained from the XRD pattern, $\Theta$ is the diffraction

angle, d is the averaged dimension of crystallites in nanometers and Λis the wavelength of X-ray used which can be obtained from Bragg's equation, $n\Lambda=2d\sin\Theta$, where n=1; Θ and d can be obtained from XRD pattern.

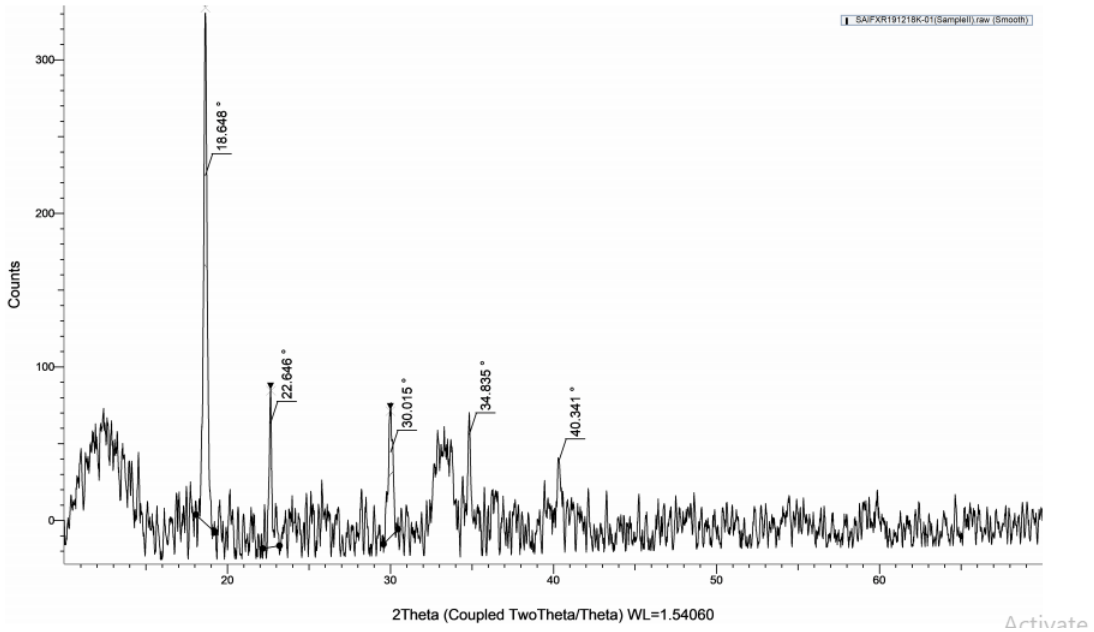



**Fig d: XRD of $Co_3O_4$ NPs obtained by chemical reduction**

The high intensity Peak was observed at 2Θ valued of 18.648◦. The peak broadening in the XRD Pattern indicates the presents of small nanocrystals. Therefore, according to Scherrer equation,

2Θ=18.648˚, Θ=9.324˚

Λ=1.54062nm β=0.222

Therefore,

$$D=\frac{0.9\times1.54062\times180}{0.222\times\cos(9.324)\times3.14\times10}=36.28\text{nm}$$

The size of the Co nanoparticle calculated from the above spectrum using the Scherrer equation is equal to 36.28nm

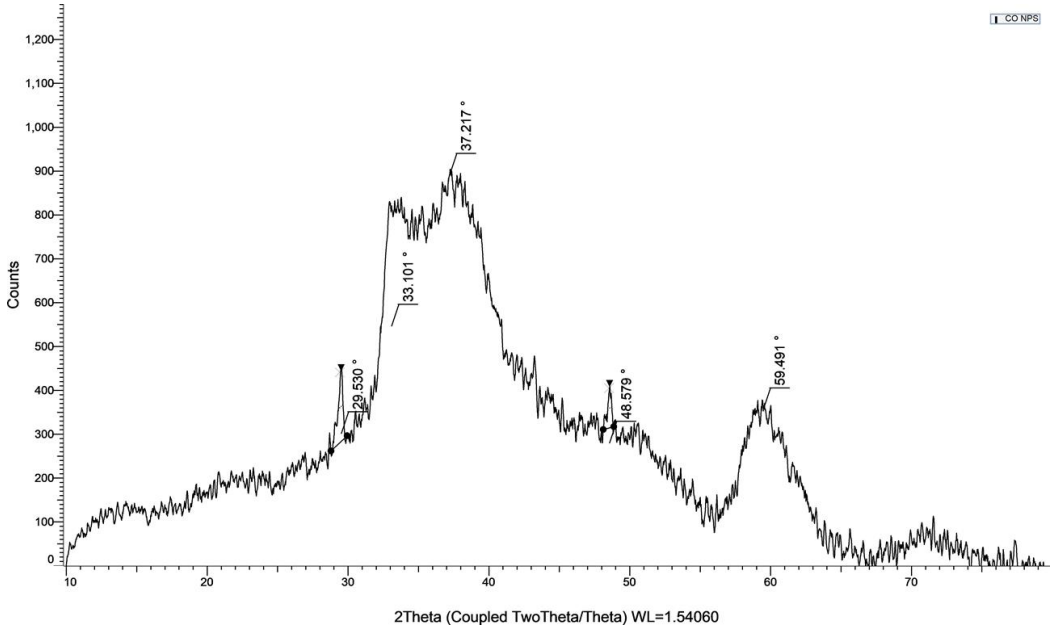



**Fig e: XRD of $Co_3O_4$ NPs obtained by replacing starch and ascorbic acid**

The high intensity Peak was observed at 2Θ valued of 59.491˚. The peak broadening in the XRD Pattern indicates the presents of small nanocrystals. Therefore, according to Scherrer equation,

$2\Theta=29.530^{\circ}$, $\Theta=14.765^{\circ}$

$\Lambda=1.54062nm$, $\beta=0.365$

Therefore,

$$D=\frac{0.9x1.54062x180}{0.365\times\cos(14.765)\times 3.14\times 10}=22.52nm$$

The size of the Co nanoparticle calculated from the above spectrum using the Scherrer equation is equal to 22.52nm

Since there is much difference in the size of the synthesized nanoparticles, aloe vera extract can be used as an alternate way to synthesis the Co nanoparticles.

# CHAPTER IV

# CONCLUSION

The Nickel and Cobalt oxide nanoparticles were synthesized from $NiSO_4$. $6H_2O$ and $Co(NO_3)_2.6H_2O$ respectively, by chemical reduction method, using NaOH to regulate pH, ascorbic acid as a reducing agent and starch as capping agent.

Characterization of nanoparticles is done by UV-Visible spectroscopy and X-ray Diffraction (XRD). From the XRD result it has been found that size of the Nickel nanoparticle is 45.01nm.

Cobalt oxide nanoparticles were synthesized by two different methods. Chemically reduced Cobalt oxide NPs shows a particle size of 36.28nm and an absorbance peaks at 305nm due to a phenomenon called surface plasmon resonance effect (SPRE).

Cobalt oxide nanoparticle obtained by replacing starch and ascorbic acid by Aloe vera extract shows a particle size of 22.52 nm and shows absorbance peaks at 310nm. Aloe vera extract with its jelly like nature and excellent antioxidant property can effectively replace Starch and Ascorbic acid.

The fluorescence, the UV – Visible spectrum and XRD studies showed that the present study illustrates a simple and convenient method for synthesis Cobalt oxide nanoparticles through the reduction of Cobalt salts using Aloe Vera extract.

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