PROJECT REPORT

On

"SYNTHESIS AND CHARACTERIZATION OF METALLIC COPPER AND BIMETALLIC COPPER-SILVER NANOPARTICLES BY CHEMICAL REDUCTION METHOD "

Submitted by

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In partial fulfillment for the award of the
BSc Degree in Chemistry

POST GRADUATE AND RESEARCH
DEPARTMENT OF CHEMISTRY

ST. TERESA'S COLLEGE (AUTONOMOUS)
ERNAKULAM
2018-2019

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B.Sc. CHEMISTRY PROJECT REPORT

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This is to certify that the project "**SYNTHESIS AND CHARACTERIZATION OF METALLIC COPPER AND BIMETALLIC COPPER-SILVER NANOPARTICLES BY CHEMICAL REDUCTION METHOD**" is the work done by **DEVIKA V.S., SANDRA ANTONY, JOICE ANN JOSEPH** .

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Submitted to the Examination of Bachelor's Degree in Chemistry
Date:……………
Examiners : ………………………………………

DECLARATION

I hereby declare that the project work entitled "**SYNTHESIS AND CHARACTERIZATION OF METALLIC COPPER AND BIMETALLIC COPPER-SILVER NANOPARTICLES BY CHEMICAL REDUCTION METHOD**" submitted to Department of Chemistry, St. Teresa's College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, is a record of an original work done by me under the guidance of **MARY LINCY K.A**, Assistant Professor, Department of Chemistry, St. Teresa's College (Autonomous), Ernakulam and this project work is submitted in the partial fulfillment of the requirements for the award of the degree of Bachelor of Science in Chemistry.

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Acknowledgements

First of all, we am highly thankfull to God Almighty for his continuous blessings for the successful completion of my project.

We wish to express my profound sense of gratitude to Mrs. Mary Lincy K.A my guide and Assistant Professor of Department of Chemistry, St. Teresa's College, for her valuable guidance personal attention encouragement and meaningfull sugestions.

We take this opportunity to convey my gratefulness to Mrs. Anitta Antony, ,Research fellow, St .Teresa's College, for the advice and help received from her.

We are also thankfull to Dr. Ushamani M , Head of Department of Chemistry , St.Teresas College ,Ernakulam .

We would like to express my gratitude to all our teachers and non-teaching staffs for the whole hearted help throughout our project.

We are greatfull to the Principal Dr..Sajimol Augustine and Director Rev. Sr..Dr. Vinitha, St.Teresa's College, Ernakulam for being the pillars of support and providing good infrastructure for the study and development of students.

We thank STIC, Cochin University of Science and Technology, Kalamassery and also Dr. Helvin Vincent, Department of Zoology, St Teresa's College ,for the facilities provided for the analysis of my sample .

Last but not the least , We are greatfull to my loving family and friends for the care and concern they provide to follow my passion .

Place: ERNAKULAM   DEVIKA V.S
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Chapter 1

Introduction

Nanoscience and nanotechnology refers to the control and manipulation of matter at nanometer dimensions. This control has made it possible to have life, which is a collection of most efficient nanoscale processes. The best eco-friendly and efficient processes must learn from nature. When we explore life around us, it is found that organization of nanomaterials is central to biology. Architectures made by organisms are all based on nanoassemblies .Today we know that it is possible to use biological processes to make artificial nanostructures. Chemically synthesized nanostructures have been used at various stages of civilization.

Scientists have adopted the Greek word 'nano' as a prefix to mean one billionth of unit of a measure. Nanoscience and nanotechnology are the study and the application of extremely small things and can be used across all other science fields, such as chemistry, biology, physics, material science and engineering.

NANO – The Beginning

Many nano forms of matter exist around us .One of the earliest nano- sized objects known to us was made of gold. Faraday prepared colloidal gold in 1856 and called it 'divided metals'. In his diary he called the particles he made 'the divided state of gold'.

Colloidal gold has been incorporated in glasses and vases to give them color. The oldest of these is the fourth Century AD Lycurgus cup made by the Romans. The cup appears red in transmitted light (if a light source is kept within the cup) and appears green in reflected light (if light source is outside)

THE LYCURGUS CUP

Nature makes nano objects of varying kind. Magnetite (Fe_3O_4) particles of nanometer size are made by the bacteria, magnetosperillummagnetotacticum.

Nanoscience and nanotechnology involves the ability to see and control individual atoms and molecules. Everything on earth is made up of atom- the food we eat, the cloths we wear, the buildings and houses we live in and our own bodies. But an atom is so small to see with our naked eyes. Alternate sized gold and silver particles created colors in the stained glass windows of the medieval churches a hundreds of years ago. The artist then didn't know that the process they used to create these beautiful works of art actually led to changes in the composition of the materials they were working with.[1]

Today's scientist and engineers are finding a wide variety of ways to deliberately make materials at a nanoscale to take advantages of theirenhanced properties such as higher strength , lighter weights ,increased control of light spectrum, and greater chemical reactivity than their large counterparts.

1.1. APPLICATIONS OF NANOTECHCOLOGY

The phenomenal expansion and growth of nanoscience and nanotechnology has been historically unprecedented. Technological revolutions have shown that pioneering scientific discoveries have the

potential to pave the way for radically innovative and integrated approaches and for providing new solutions. Nanotechnology unlike any other technology can find applications in virtually all areas of human life. Because of its distinctiveness and pervasiveness it has the potential to revolutionize the way we live, think, behave and act.[2]

Medicine

Researchers are developing customized nanoparticles the size of molecules that can deliver drugs directly to diseased cells in your body. When it's perfected, this method should greatly reduce the damage treatment such as chemotherapy does to a patient's healthy cells.

 • Electronics

Nanotechnology holds some answers for how we might increase the capabilities of electronics devices while we reduce their weight and power consumption.

• Food

Nanotechnology is having an impact on several aspects of food science, from how food is grown to how it is packaged. Companies are developing nanomaterials that will make a difference not only in the taste of food, but also in food safety, and the health benefits that food delivers.

• Fuel Cells

Nanotechnology is being used to reduce the cost of catalysts used in fuel cells to produce hydrogen ions from fuel such as methanol and to improve the efficiency of membranes used in fuel cells to separate hydrogen ions from other gases such as oxygen.

• Solar Cells

Companies have developed nanotech solar cells that can be manufactured at significantly lower cost than conventional solar cells.

• Batteries

Companies are currently developing batteries using nanomaterials. One such battery will be a good as new after sitting on the shelf for decades. Another battery can be recharged significantly faster than conventional batteries.

• Space

Nanotechnology may hold the key to making space-flight more practical. Advancements in nanomaterials make lightweight spacecraft and a cable for the space elevator possible. By significantly reducing the amount of rocket fuel required, these advances could lower the cost of reaching orbit and traveling in space.

• Fuels

Nanotechnology can address the shortage of fossil fuels such as diesel and gasoline by making the production of fuels from low grade raw materials

economical, increasing the mileage of engines, and making the production of fuels from normal raw materials more efficient.

• Better Air Quality

Nanotechnology can improve the performance of catalysts used to transform vapors escaping from cars or industrial plants into harmless gasses. That's because catalysts made from nanoparticles have a greater surface area to interact with the reacting chemicals than catalysts made from larger particles. The larger surface area allows more chemicals to interact with the catalyst simultaneously, which makes the catalyst more effective.

• Cleaner Water

Nanotechnology is being used to develop solutions to three very different problems in water quality. One challenge is the removal of industrial wastes, such as a cleaning solvent called TCE, from groundwater. Nanoparticles can be used. Studies have shown that this method can be used successfully to reach contaminates dispersed in underground ponds and at much lower cost than methods which require pumping the water out of the ground for treatment

• Chemical Sensors

Nanotechnology can enable sensors to detect very small amounts of chemical vapors. Various types of detecting elements, such as carbon

nanotubes, zinc oxide nanowires or palladium nanoparticles can be used in nanotechnology-based sensors. Because of the small size of nanotubes, nanowires, or nanoparticles, a few gas molecules are sufficient to change the electrical properties of the sensing elements. This allows the detection of a very low concentration of chemical vapors.

• Sporting Goods

If you're a tennis or golf fan, you'll be glad to hear that even sporting goods has wandered into the nano realm. Current nanotechnology applications in the sports arena include increasing the strength of tennis racquets, filling any imperfections in club shaft materials and reducing the rate at which air leaks from tennis balls

• Fabric

Making composite fabric with nano-sized particles or fibers allows improvement of fabric properties without a significant increase in weight, thickness, or stiffness as might have been the case with previously-used techniques.

1.2. NANOMATERIALS AND ITS CLASSIFICATION

Nanomaterials are chemical substances or materials that are manufactured and used at a very small scale. Nanomaterials are developed to exhibit novel characteristics compared to the same material without nanoscale

features, such as increased strength, chemical reactivity or conductivity.
[3]

CLASSIFICATION:

1.2.1. **Based on configuration**

Carbon Based Materials

These nanomaterials are composed mostly of carbon, most commonly taking the form of a hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes, while cylindrical ones are called nanotubes. These particles have many potential applications, including improved films and coatings, stronger and lighter materials, and applications in electronics.

Metal Based Materials

These nanomaterials include quantum dots, nanogold, nanosilver and metal oxides, such as titanium dioxide. A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, and whose size is on the order of a few nanometers to a few hundred nanometers. Changing the size of quantum dots changes their optical properties.

Dendrimers

These nanomaterials are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can be

tailored to perform specific chemical functions. This property could also be useful for catalysis. Also, because three-dimensional dendrimers contain interior cavities into which other molecules could be placed, they may be useful for drug delivery.

Composites

Composites combine nanoparticles with other nanoparticles or with larger, bulk-type materials. Nanoparticles, such as nanosized clays, are already being added to products ranging from auto parts to packaging materials, to enhance mechanical, thermal, barrier, and flame-retardant properties.

1.2.2. Based on dimension

Zero-dimension in 0-D system (quantum dot), the electrons are confined in their motion in all three directions. Example: spheres and nanoclusters. 1.2.2 one-dimension In 1-D system (quantum wire), the electrons are free to travel in one direction and confined in the other two directions. Example: Nanofibers, nanowires, nanorods, etc. 1.2.3 Two-dimension In 2-D system (quantum well), the electrons can easily move in two directions and are confined in one direction. Example: Nanofilms, nanoplates and branched structures. 1.2.4 Three dimension in 3-D system (bulk), the electrons are free to move in all three directions and there are no confinement and limitations. Example: powders, multilayer, fibrous

and poly crystalline materials wherein nonstructural elements of 0-D, 1-D and 2-D are closely related with each other and form interfaces.

1.2.3. Based on origin

Natural: nanomaterials which are belonging to resourses of nature are natural nanomaterials. Example: virus, protein molecules including antibody originated from nature are some natural nanostructured materials. Minerals such as clay, natural colloids (milk, blood, fog, gelatin), mineralized natural materials such as shells, bones and corals, insect wings and opalus spider silk, lotus leaves etc.

Artificial: nanomaterials that are prepared deliberately through a well defined mechanical and fabrication process. Examples: carbon nanotubes, semiconductor nanoparticles like quantum dots etc.

1.3. VARIOUS METHODS OF SYNTHESIS OF NANOMATERIALS.

1.3.1. Chemical reduction

Currently developed synthesis methods for copper nanoparticles include chemical reduction, thermal deposition, polyol, laser ablation, electron beam irradiation and an in situ chemical synthesis route. Among these methods, chemical reduction is the most preferred, because this method is simple and economical, and it can realize better size and size distribution control by optimizing the experimental parameters, such as the molar ration of the capping agent with the precursor salt and the ratio of the

reducing agent with the precursor salt. A chemical reduction method usually involves the reduction of metal salts in some type of solvent and a separate reducing agent.

1.3.2. Physical method

Evaporation-condensation and laser ablation are the most important physical approaches. The absence of solvent contamination in the prepared thin films and the uniformity of nanoparticles distribution are the physical advantages of physical synthesis methods in comparison with the chemical process. Physical synthesis of silver nanoparticles using a tube furnace at atmospheric pressure has some disadvantages for example tube furnace occupies a large space consumes a great amount of energy while rising the environmental temperature around the source material and requires a lot of time to achieve thermalstability. Moreover, a typical furnace requires power consumption of more than several kilowatts and a preheating time of ten minutes to reach a stable operating temperature. This makes possible the formation of small particles at high concentration. The particle generation is very stable, because the temperature of the heater surface does not fluctuate with time. This physical method can be useful as a nanoparticle generator for long term experiments for inhalation toxicity studies and as calibration device for nanoparticle measurement equipment.

1.3.3. Biosynthesis

Many bacteria,fungi and plants have shown the ability to synthesis metallic nanoparticles and have their own advantages and disadvantages.Intercelular or extracellular synthesis time,ease of extraction and percentage synthesized versus percentage removed from sample ratio ,all play an important role in biological nanoparticle production.

Naturally biogenic metallic synthesis can be split into two categories. The first is bioreduction in which metal ions are chemically reduced into more stable forms biologically. Many organisms have the ability to utilize dissimilatory metal reduction, in which the reduction of a metal ion is coupled with the oxidation of an enzyme. This results in stable and inert metallic nanoparticles that can then be safely removed from a contaminated sample. The second category is bio-sorption. This involves the binding of metal ions from an aqueous or soil sample onto the organism itself,such as on the cell wall, and does not require the input of energy.Certain bacteria, fungi and plants express pesticides or have a modified cell wall which binds to metal ions and these are able to form stable complexes in the form of nanoparticles.

1.3.4. Nanoparticle synthesis by bacteria

Research has focused heavily on prokaryotes as a means of synthesizing metallic nanoparticles. Due to their abundance in environment and their ability to adapt to extreme condition, bacteria are a good choice for study.Growth conditions such as temperature,oxygenation and incubation time can be easily controlled.

1.3.5. Nanoparticle synthesis by fungi

The use of fungi in producing metallic nanoparticles has received significant interest as they offer certain advantages over the use of bacteria for the synthesis of nanoparticles.The ease of scaling up and downstream processing,the economic feasibility and the presence of mycelia offering an increased surface area, are important advantages to consider.

1.3.6. Nanoparticle synthesis by plants

Bacteria and fungi have been studied extensively in the past few decades for their ability to synthesis metallic nanoparticles, however there has been less of a focus on plants in this matter. An increasing amount of research is being performed on the green synthesis of metallic nanoparticles using plants or plant extracts. A very important aspect of using plants instead of bacteria or fungi for nanoparticles production is the lack of pathogenicity.

1.4 COPPER NANOPARTICLES

Copper is a Block D, Period 4 element. It is a ductile metal with very high thermal and electrical conductivity. The morphology of copper nanoparticles is

round, and they appear as a brown to black powder. Copper is found to be too soft for some applications, and hence it is often combined with other metals to form numerous alloys such as brass, which is a copper-zinc alloy. Copper nanoparticles are graded as highly flammable solids, therefore they must be stored away from sources of ignition. They are also known to be very toxic to aquatic life.[4]

1.4.1.Chemical Properties

The chemical properties of copper nanoparticles are outlined in the following table.

Chemical Data	
Chemical symbol	Cu
CAS No.	7440-50-8
Group	11
Electronic configuration	[Ar] $3d^{10}$ $4s^1$

1.4.2. Physical Properties

The physical properties of copper nanoparticles are given in the following table.

Properties	Metric	Imperial

Density	8.94 g/cm^3	0.00032 lb/in^3
Molar mass	63.55 g/mol	-

1.4.3. Thermal Properties

The thermal properties of copper nanoparticles are provided in the table below.

Properties	Metric	Imperial
Melting point	1083°C	1981.4°F
Boiling point	2567°C	4652.6°F

1.4.4. Applications

The key applications of copper nanoparticles are listed below:

•Acts as an anti-biotic, anti-microbial, and anti-fungal agent .

•Copper diet supplements with efficient delivery characteristics

•High strength metals and alloys

•EMI shielding

•Heat sinks and highly thermal conductive materials

•Efficient catalyst for chemical reactions.

•As sintering additives and capacitor materials

•Superficial conductive coating processing of metal and non-ferrous metal

•As nanometal lubricant additives

Copper nanoparticles application research is ongoing to discover their potential dielectric, magnetic, electrical, optical, imaging, catalytic, biomedical and bioscience properties.

1.5   COPPER – SILVER NANOPARTICLES

The preparation of Cu nanoparticles is problematic due to their easy oxidation. However, one can prepare CuO nanoparticles that are of great interest due to their potential applications in a wide variety of areas including electronic and optoelectronic devices. The behavior of bulk alloys of copper and silver is generally well known as they form a eutectic system. The Ag-Cu system exhibits a limited mutual solubility of Ag-and Cu-rich phases in solid.

The silver nanoparticle has many applications due to the large degree of commercialization. Silver (Ag) is an attractive material for its distinctive properties, such as good conductivity, chemical stability, catalytic activity, and antimicrobial activity. Ag nanoparticles are used in antimicrobial applications since the antimicrobial effect of Ag ions is well known.[5]

Ag NP applications include the medical field as well as in water and air filtration. Furthermore, silver nanoparticles have individual plasmon optical spectra properties which allow being silver nanoparticles used in biosensing application

Silver (Ag) and copper (Cu) nanoparticles have shown great potential in variety applications due to their excellent electrical and thermal properties resulting high demand in the market. Decreasing in size to nanometer scale has shown distinct improvement in these inherent properties due to larger surface-to-volume ratio. Ag and Cu nanoparticles are also shown higher surface reactivity, and therefore being used to improve interfacial and catalytic process. Their melting points have also dramatically decreased compared with bulk and thus can be processed at relatively low temperature. Besides, regularly alloying Ag into Cu to create Ag–Cu alloy nanoparticles could be used to improve fast oxidizing property of Cu nanoparticles. There are varieties methods have been reported on the synthesis of Ag, Cu, and Ag–Cu alloy nanoparticles.

1.6. CHARACTERISATION OF NANOPARTICLES

Nanoparticles have been characterized by XRD and UV-Visible Techniques.

1.6.1. X-RAY DIFFRACTION (XRD) TECHNIQUE

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.[6]

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.[7]

The average crystalline size of aparticle can be determined using X-Ray Diffraction studies using the Debye-Scherrer equation :

Crystalline size D $=(0.9\lambda) / (d \cos \theta)$

Where λ is the wavelength of X- ray$=1.54$Å ,d is the intensity of the peak and θ is the angle of diffraction .

All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample, and the diffracted rays are collected. A key component of all diffraction is the angle between the incident and diffracted rays. Powder and single crystal diffraction vary in instrumentation beyond this.

X-ray Powder Diffraction (XRD) Instrumentation - How Does It Work?

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector

Bruker's X-ray Diffraction D8-Discover instrument.

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra

consist of several components, the most common being Kα and Kβ. Kα consists, in part, of Kα1 and Kα2. Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Kα1and Kα2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuKα radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

X-ray powder diffractogram. Peak positions occur where the X-ray beam has been diffracted by the crystal lattice. The unique set of d-spacings derived from this patter can be used to 'fingerprint' the mineral.[16]

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates

at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at 2θ from ~5° to 70°, angles that are preset in the X-ray scan.

Applications

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

Other applications include:

•Characterization of crystalline materials

•Identification of fine-grained minerals such as clays and mixed layer

  clays that are difficult to determine optically

•Determination of unit cell dimensions

•Measurement of sample purity

1.6.2   ULTRA VIOLET SPECTROSCOPY (ELECTRONIC SPECTROMETRY)

Electromagnetic radiation in the 10-800nm region is capable of interacting with molecules to give rise to electronic transitions. The 10-400nm constitutes the ultraviolet (UV) region and the 400-800nm constitutes the visible region of the electromagnetic spectrum. Ultraviolet radiation having wavelengths less than 200nm is difficult to handle and is not commonly used a s a routine tool for structural analysis.

Energy is in 200-800nm that is those in the near -UV and visible regions , are sufficient to excite an electron to a higher electronic energy level. Consequently absorption spectroscopy carried out in this region is sometimes electronic spectroscopy or UV visible spectroscopy. In short electronic spectroscopy involves the study of electronic transitions from lower to higher quantised energy levels induced in a molecular species by absorption of energy in the UV region. The ultraviolet spectrometers consists of a light source, reference and sample beams a monochromatic and detector.

In a typical UV visible absorption experiment a beam of monochromatic light split into two beams : one of them is passed through the sample and the reference. After transition to the sample and reference, the two beams are directed back to the detectors where they are compared. The difference between the signals is the basis of the measurement .UV-Vis spectroscopy offers a relatively straight forward and effective way for quantitatively characterising both organic and inorganic nano materials.[8],[9].

Chapter 2

Materials and Methods

MATERIALS REQUIRED:

- Copper (II) Sulphate pentahydrate (CuSO$_4$.5H$_2$O)

- Silver Nitrate (AgNO$_3$)

- Tri- sodium citrate dihydrate (C$_6$H$_5$Na$_3$O$_7$.2H$_2$O)

- Sodium borohydride(NaBH$_4$)

- Standard flask

- Beaker

- Measuring cylinder

- Watch glass

- Dropper

- Funnel

- Stirrer

EXPERIMENT:

2.1 PREPARATION OF STOCK SOLUTIONS :

1M of CuSO$_4$ (62.42g of CuSO$_4$) was prepared in a 250 mL standard flask,1M AgNO$_3$ was prepared in a 50 mL standard flask ,2M NaBH$_4$ (1.89g) of NaBH$_4$ was prepared in a 25 mL standard flask and the capping agent Tri-sodium citrate

dihydrate ($C_6H_5Na_3O_7.2H_2O$) was prepared in a 25mL standard flask. All solutions were made using distilled water.

2.2 PREPARATION OF COPPER NANO PARTICLES

In a dry 100ml beaker 25ml of 1M $CuSO_4$ solution was added, covered with an aluminium foil and kept in stirrer. 5ml of 1M trisodium citrate, was added. 5ml of 2M $NaBH_4$ was added drop wise till the colour changes to dark yellow. This indicates the formation of copper nano particles. The solution was kept in the stirrer for about 15mins till the colour changes to dark yellow. The nanoparticles formed were analyzed using X-Ray Diffraction and UV-Visible spectroscopic studies. [10].

2.3 PREPARATION OF Cu-Ag NANOPARTICLES .

Copper nanoparticles were prepared in aqueous solution by chemical reduction technique, using sodium borohydride as reducing agent to reduce copper sulphate to metallic nano copper. In a typical set 25 mL of 1M $CuSO_4$ solution was mixed with 25 mL $AgNO_3$ solution in a dry 100ml beaker and 5 mL of 1M trisodium citrate solution was added, which allow the capping of nanoparticles.5 mL of 2M aqueous solution of $NaBH_4$ was then added drop wise to it under constant stirring for 25 minutes. The colour of the solution was changed to dark yellow on gradual addition of reducing agent indicating the formation of Cu nanoparticles. The particles formed was separated by filtration using a whattman filter paper and dried. The particles were analysed by X-ray Diffraction studies and UV-Visible spectroscopic studies [11].

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Chapter 3

Results and discussion

Many methods can be used for the preparation of copper nanoparticles, but a few routs are eco-friendly. Production of pure nanoparticles is rare, unless the whole procedure is carried out under an inert atmosphere. Nanoparticles are usually protected with a capping agent in order to minimize oxidation and control the growth of a crystal by decreasing the surface energies of crystals. However, the capping agents or stabilizers can significantly reduce the oxidation but may not prevent it completely because of their molecular motion.

In the present study copper nanoparticles and bimetallic silver-copper nanoparticles were synthesized by chemical reduction. In chemical reduction method copper nanoparticles were obtained by the reduction of copper sulphate solution using Sodium borohydride as the reducing agent and Trisodium citrate as the capping agent. This method was simple economic and rapid approach to synthesize copper nanoparticles. Trisodium citrate was used as the capping agent, in order to prevent the oxidation and agglomeration.

In chemical reduction, a visible colour change was observed indicating the formation of copper nanoparticles and silver-copper nanoparticles.

Nanoparticles prepared in the laboratory were characterized using XRD technique and UV-Visible spectroscopic technique[11].

From the X-Ray diffraction data the average crystalline size is calculated using the Debye-Scherrer equation ;
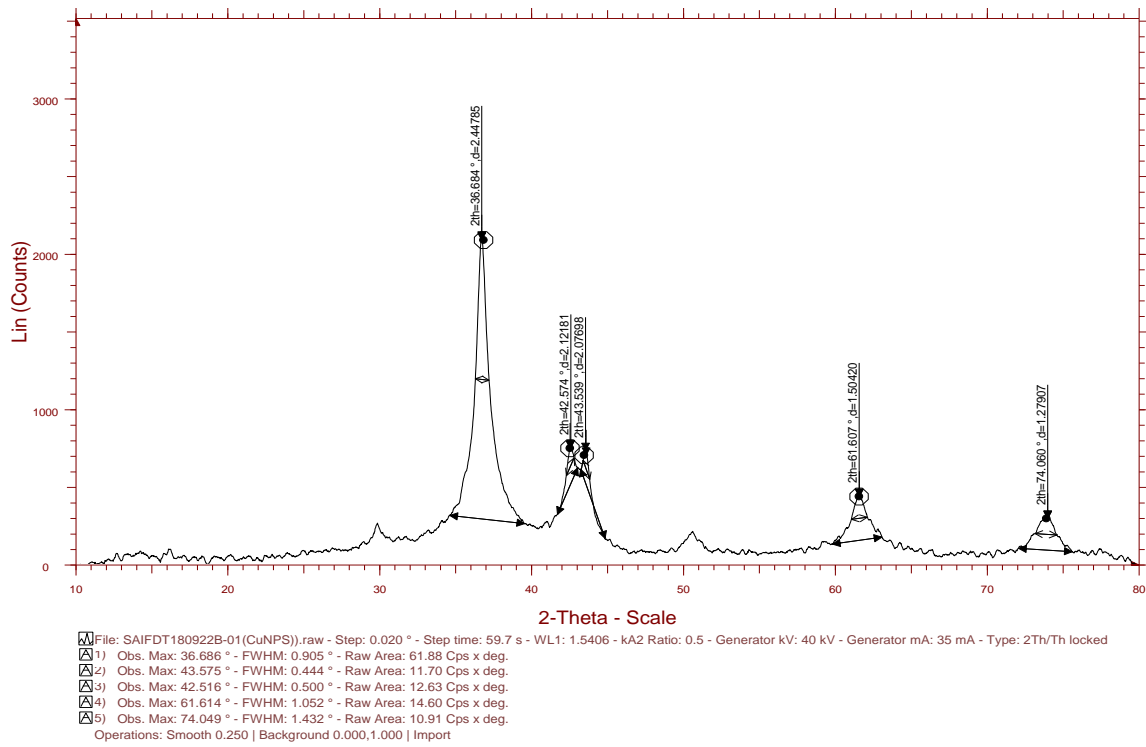
$$\text{Particle size }, D = (0.9 * \Lambda) / (d \cos\theta)$$

Where , Λ = wavelength of radiation used =1.54Å , d is the intensity of the peak and θ is the angle of diffraction .

3.1 . DETERMINATION OF PARTICLE SIZE

3.1.1 COPPER CHEMICAL REDUCTION

CuNPS

File: SAIFDT180922B-01(CuNPS)).raw - Step: 0.020 ° - Step time: 59.7 s - WL1: 1.5406 - kA2 Ratio: 0.5 - Generator kV: 40 kV - Generator mA: 35 mA - Type: 2Th/Th locked
1) Obs. Max: 36.686 ° - FWHM: 0.905 ° - Raw Area: 61.88 Cps x deg.
2) Obs. Max: 43.575 ° - FWHM: 0.444 ° - Raw Area: 11.70 Cps x deg.
3) Obs. Max: 42.516 ° - FWHM: 0.500 ° - Raw Area: 12.63 Cps x deg.
4) Obs. Max: 61.614 ° - FWHM: 1.052 ° - Raw Area: 14.60 Cps x deg.
5) Obs. Max: 74.049 ° - FWHM: 1.432 ° - Raw Area: 10.91 Cps x deg.
Operations: Smooth 0.250 | Background 0.000,1.000 | Import

PEAK1

$2\Theta = 36.684$
$\Theta = 18.342$
$\cos \Theta = 0.9491$
$d = 0.905 \times 0.07146 = 0.01580$
Crystalline size $= (0.9 \lambda)/d \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(0.01580 \times 0.9491)$
$= 9.2461 \times 10^{-9} \text{nm}$

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PEAK 2

$2\Theta = 42.574$

$\Theta = 21.287$

Cos $\Theta = 0.9317$

$d = 0.500 \times 0.01746 = 8.73 \times 10^{-3}$

Crystalline size = $(0.9 \lambda)/d \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(8.73 \times 10^{-3} \times 0.9317)$

$$= 1.7040 \times 10^{-8} nm$$

PEAK3

$2\Theta = 43.539$

$\Theta = 21.7695$

Cos $\Theta = 0.92868$

$d = 0.444 \times 0.01746 = 7.7522 \times 10^{-8}$

Crystalline size = $(0.9 \lambda)/d \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(7.7522 \times 10^{-3} \times 0.92868)$

$$= 1.9251 \times 10^{-8} nm$$

PEAK4

$2\Theta = 61.607$

$\Theta = 30.8035$

Cos $\Theta = 0.8589$

$d = 1.052 \times 0.01746 = 0.01836$

Crystalline size = $(0.9 \lambda)/d \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(0.01836 \times 0.8589)$

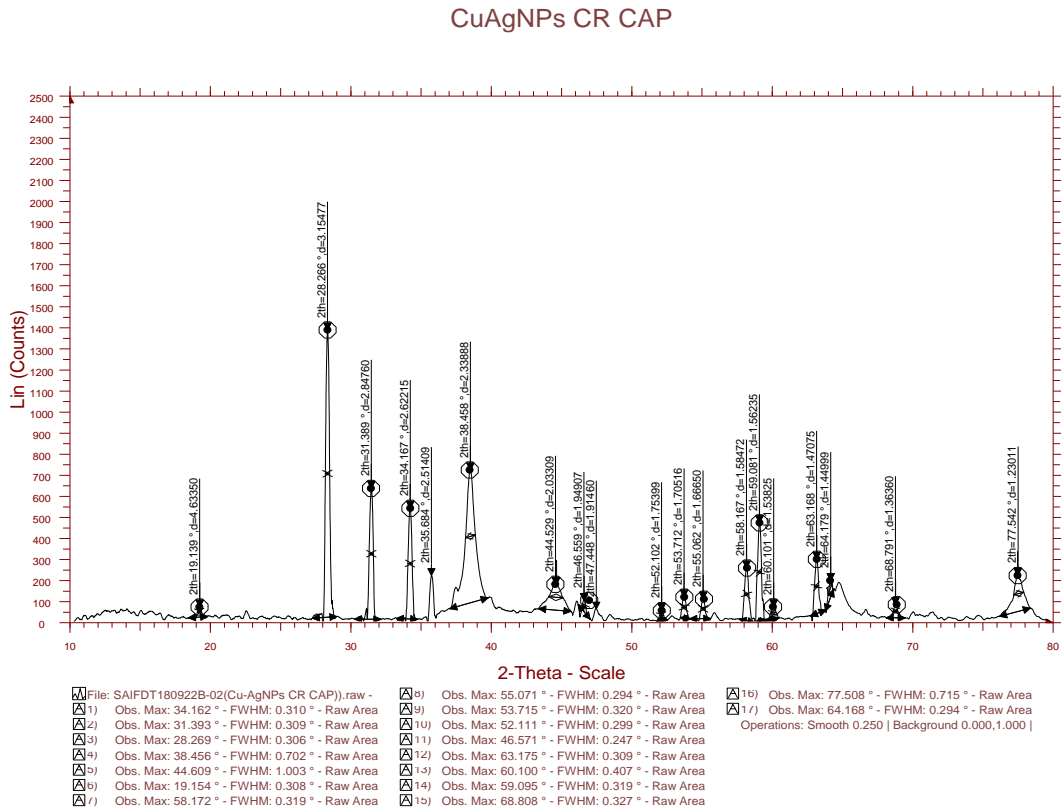$$= 8.7944 \times 10^{-9} nm$$

PEAK5

$2\Theta = 74.080$

$\Theta = 37.04$

Cos $\Theta = 0.7982$

$d = 1.432 \times 0.01746 = 0.02500$

Crystalline size = $(0.9 \lambda)/d \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(0.02500 \times 0.7982)$

$$= 6.9473 \times 10^{-9} nm$$

3.1.2 BIMETALLIC COPPER-SILVER WITH CAPPING

CuAgNPs CR CAP

PEAK1

$2\Theta = 19.139$
$\Theta = 9.5695$
$\cos \Theta = 0.9860$
$d = 0.308 \times 0.01746 = 5.37768\times10^{-3}$
Crystalline size $= (0.9\ \lambda)/d\ \cos\Theta = (\ 0.9 \times 1.54\times10^{-10}\ )/(\ 5.37768\times10^{-3} \times 0.9860\ )$

$$= 26.13689 \text{nm}$$

PEAK2

$2\Theta = 28.266$
$\Theta = 14.133$
$\cos \Theta = 0.9697$

d = 0.306 x 0.01746 = 5.34276x10^{-3}

Crystalline size = $(0.9 \lambda)/d \cos\Theta$ =(0.9 x 1.54x10^{-10})/(5.34276x10^{-3} x 0.9697)

$$= 26.75137nm$$

PEAK3

$2\Theta = 31.389$

$\Theta = 15.6945$

$\cos \Theta = 0.96271$

d = 0.702 x 0.01746 = 0.01225

Crystalline size = $(0.9 \lambda)/d \cos\Theta$ = (0.9 x 1.54x10^{-10})/(0.01225 x 0.96271)

$$= 11.7458nm$$

PEAK4

$2\Theta = 34.167$

$\Theta = 17.0835$

$\cos \Theta = 0.95587$

d = 0.310 x 0.01746 = 5.4126x10^{-3}

Crystalline size = $(0.9 \lambda)/d \cos\Theta$ = (0.9x1.54 x 10^{-10})/(5.4126x10^{-3} x 0.95587

$$= 26.7889nm$$

PEAK5

$2\Theta = 38.458$

$\Theta = 19.229$

$\cos \Theta = 0.9442$

d = 0.702 x 0.01746 = 0.01225

Crystalline size = $(0.9 \lambda)/d \cos\Theta$ = (0.9 x 1.54x10^{-10})/(0.01225 x 0.9442)

$$= 11.97604nm$$

PEAK6

$2\Theta = 44.529$

$\Theta = 22.2645$

$\cos \Theta = 0.9254$

d = 1.003 x 0.01746 = 0.01751

Crystalline size = $(0.9 \lambda)/d \cos\Theta$ = (0.9 x 1.54x10^{-10})/(0.01751 x 0.9254)

$$= 85.51998nm$$

PEAK7

$2\Theta = 46.559$
$\Theta = 23.2795$
$\text{Cos } \Theta = 0.9185$
$d = 0.247 \times 0.01746 = 4.31262 \times 10^{-3}$
$\text{Crystalline size} = (0.9\ \lambda)/d\ \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(4.3126 \times 10^{-3} \times 0.9185)$
$$= 34.9856 nm$$

PEAK8

$2\Theta = 52.102$
$\Theta = 26.051$
$\text{Cos } \Theta = 0.8984$
$d = 0.299 \times 0.01746 = 5.22054 \times 10^{-3}$
$\text{Crystalline size} = (0.9\ \lambda)/d\ \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(5.22054 \times 10^{-3} \times 0.8984)$
$$= 29.55128 nm$$

PEAK9

$2\Theta = 53.712$
$\Theta = 26.856$
$\text{Cos } \Theta = 0.8921$
$d = 0.320 \times 0.01746 = 5.5872 \times 10^{-3}$
$\text{Crystalline size} = (0.9\ \lambda)/d\ \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(5.5872 \times 10^{-3} \times 0.8921)$
$$= 27.8056 nm$$

PEAK10

$2\Theta = 55.062$
$\Theta = 27.531$
$\text{Cos } \Theta = 0.8867$
$d = 0.294 \times 0.01746 = 5.13324 \times 10^{-3}$
$\text{Crystalline size} = (0.9\ \lambda)/d\ \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(5.13324 \times 10^{-3} \times 0.8867)$
$$= 30.4484 nm$$

PEAK11

$2\Theta = 58.167$
$\Theta = 29.0835$
$\text{Cos } \Theta = 0.8739$
$d = 0.319 \times 0.01746 = 5.56974 \times 10^{-3}$
$\text{Crystalline size} = (0.9\ \lambda)/d\ \cos\Theta = (9.0 \times 1.54 \times 10^{-10})/(5.5697 \times 10^{-3} \times 0.8739)$

$$= 28.4747\text{nm}$$

PEAK12

$2\Theta = 59.081$
$\Theta = 29.5405$
$\text{Cos } \Theta = 0.8700$
$d = 0.319 \times 0.01746 = 0.02279$
Crystalline size $= (0.9\ \lambda)/d\ \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(0.02279 \times 0.8700)$
$$= 28.6025\text{nm}$$

PEAK13

$2\Theta = 60.101$
$\Theta = 30.0505$
$\text{Cos } \Theta = 0.8655$
$d = 0.407 \times 0.01746 = 7.10622 \times 10^{-3}$
Crystalline size $= (0.9\ \lambda)/d\ \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(7.10622 \times 10^{-3} \times 0.8655)$
$$= 22.5328\text{nm}$$

PEAK14

$2\Theta = 63.168$
$\Theta = 31.584$
$\text{Cos } \Theta = 0.8518$
$d = 0.309 \times 0.01746 = 5.39514 \times 10^{-3}$
Crystalline size $= (0.9\ \lambda)/d\ \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(5.39514 \times 10^{-3} \times 0.8518)$
$$= 30.1568499\text{nm}$$

PEAK15

$2\Theta = 64.179$
$\Theta = 32.0895$
$\text{Cos } \Theta = 0.84721$
$d = 0.327 \times 0.01746 = 5.7094 \times 10^{-3}$
Crystalline size $= (0.9\ \lambda)/d\ \cos\Theta = (0.9 \times 1.54 \times 10^{-10})/(5.7094 \times 10^{-3} \times 0.84721$
$= 31.8695\text{nm}$

PEAK16

$2\Theta = 68.791$
$\Theta = 34.3955$
$\text{Cos } \Theta = 0.82515$

d = 0.327 x 0.01746 = 5.70942×10^{-3}

Crystalline size = $(0.9 \ \lambda)/d \ \cos\Theta$ = $(0.9 \ x \ 1.54 \times 10^{-10})/(5.70942 \times 10^{-3} \ x \ 0.82515)$

$$= 29.41942 nm$$

PEAK17

$2\Theta = 77.542$

$\Theta = 38.771$

$\cos \Theta = 0.7796$

d = 0.715 x 0.01746 = 0.01248

Crystalline size = $(0.9 \ \lambda)/d \ \cos\Theta$ = $(0.9 \ x \ 1.54 \times 10^{-10})/(0.01248 \ x \ 0.7796)$

$$= 14.2400 nm$$

SAMPLES	2Ө VALUES OF THE INTENSE PEAK (Deg)	FWHM OF THE INTENSE PEAK (Deg)	CRYSTALLINE SIZE , D (nm)	AVERAGE CRYSTALLINE SIZE (nm)
COPPER CHEMICAL REDUCTION	36.684	0.905	8.7156	10.6600
	42.574	0.500	15.8766	
	43.539	0.444	17.8790	
	61.607	1.052	5.2852	
	74.060	1.432	5.5437	
BIMETALLIC COPPER-SILVER CHEMICAL REDUCTION (with cap)				
	28.266	0.306	**26.7513**	29.2356
	31.389	0.702	11.7458	
	34.167	0.310	26.7889	
	38.458	0.702	11.9760	
	44.529	1.003	85.5199	
	46.559	0.247	34.9865	
	52.102	0.299	29.5512	
	53.712	0.320	27.8056	
	55.062	0.294	30.4484	
	58.167	0.319	28.4747	
	59.081	0.319	28.6025	
	60.101	0.407	22.5328	
	63.168	0.309	30.1568	
	64.179	0.294	31.8695	
	68.791	0.327	29.4194	
	77.542	0.715	14.2400	

Table .1 , showing the average crystalline size of copper , copper oxide , and silver nanoparticles by different methods .

3.2 . CHARACTERISATION OF PARTICLES BY UV-VISIBLE SPECTROSCOPY

3.2.1 Characterization of copper nanoparticles by chemical reduction.
The UV-Visible spectra of copper nanoparticles obtained by chemical reduction showed a peak approximately at 650 nm , clearly showing the presence of formation of Copper nanoparticles.
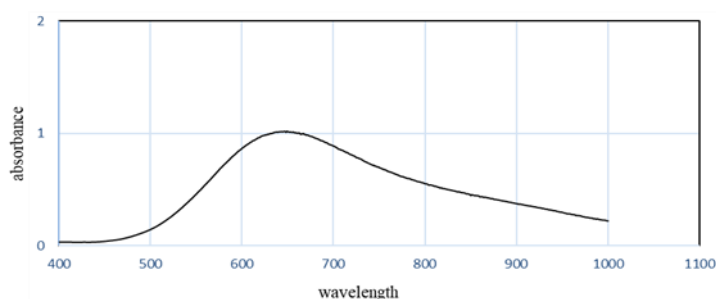

Fig 2.1: UV-Visible spectrum of copper nanoparticles by chemical reduction

3.2.2 Characterization of Bimetallic silver-copper nanoparticles.

UV-Visible spectrum of Ag-CuO nanoparticles showed characteristic peaks at 300 nm and 650 nm , which shows the presence of both silver and copper (oxide) nanoparticles respectively .
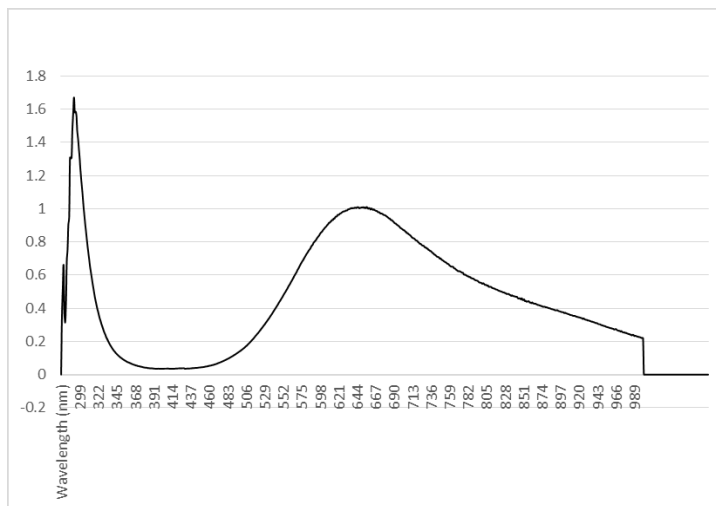
Fig 2.2: UV-Visible spectrum of Ag-CuO nanoparticles by chemical reduction.

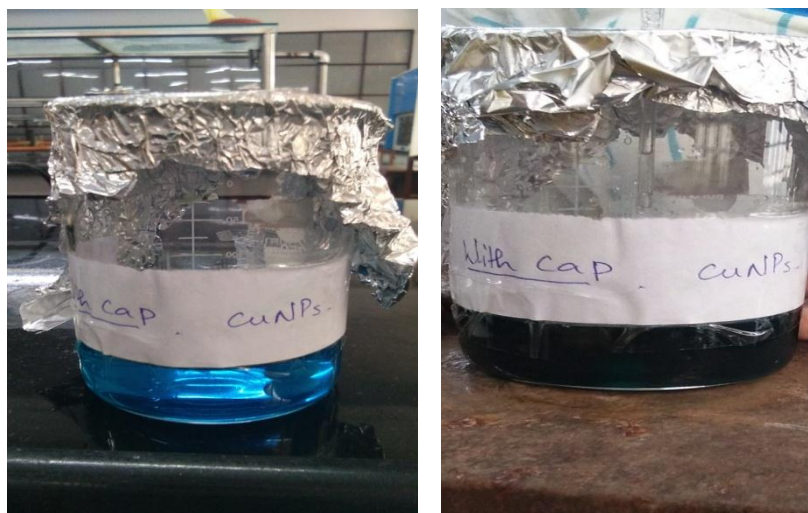## 3.3 VISIBLE OBSERVATIONS

CHEMICAL REDUCTION METHOD

Fig : 1 represents when 25ml of 1M $CuSO_4$ solution was added, covered with an aluminium foil and 5ml of 1M trisodium citrate, was added. 5ml of

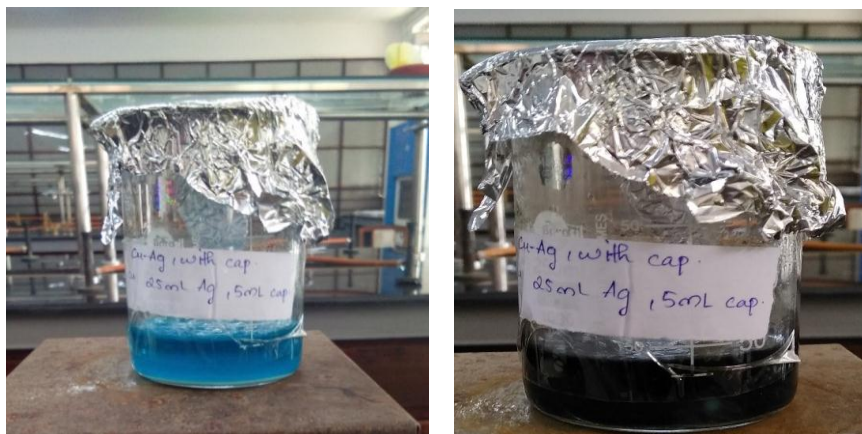2M NaBH₄ was added drop wise till the colour changes. This indicates the formation of copper nano particles. \

Fig : 2 represents when 25 mL of 1M CuSO₄ solution was mixed with 25 mL AgNO₃ solution in a dry 100ml beaker and 5 mL of 1M trisodium citrate solution was added, which allow the capping of nanoparticles.5 mL of 2M *aqueous solution of NaBH₄ was then added drop wise till the colour changes*

.

Chapter 4

Conclusions

Nanotechnology has a great importance in the field of modern research. It can be applied in almost all fields such as chemical industry, pharmaceuticals, biomedical science, drug and gene delivery, cosmetics, environmental health, space industries, etc. It is also used for the treatment of cancer, diabetes, allergies and inflammation. Over the past few years metal nanoparticles have been of a great interest for the researchers because of their great potential application in various fields such as magnetic recording media or micro electronics , catalysis , thermal and electrical conductivity, anti-bacterial and anti- fungal properties and so on[12] .

Silver and copper nanoparticles are gaining great importance due to their excellent anti-bacterial, anti-fungal, anti-biotic properties, catalytic, magnetic, electrical and optical activity, which is different from that of the bulk material. It is seen that the metal nanoparticles (Ag, Cu, CuO, Au) exhibit a wide spectrum of anti bacterial activity against different species of microorganisms. The availability and low cost of synthesis made copper a better choice to work with.

 The combination of two different metal nanoparticles is known as bimetallic nanoparticles .In this work we made Cu-Ag bimetallic nanoparticles due to their wide range of application. For that we prepared copper nanoparticles by chemical reduction using Sodium borohydride as the reducing agent, and Trisodium citrate as the capping or stabilizing agent[13]. The average crystalline size of copper nanoparticles formed was determined as 10.660 nm by X-ray diffraction studies.

The same reagents were used to synthesise bimetallic copper and copper-silver nanoparticles, and average crystalline size was determined as 27.7129 nm for copper oxide nanoparticles and 35.4732 nm for silver nanoparticles.

UV-Visible studies were carried out with very diluted (milli molar) concentrations , and they revealed the presence of copper and silver nanoparticles in respective samples. UV-Visible spectra of copper nanoparticles by chemical reduction showed a peak at 650 nm and in bimetallic silver and copper oxide sample it show a peak at 300 nm and 650 nm revealing the presence of both silver and copper nanoparticles[14].

Thus, the present study gives us a low cost and relatively eco-friendly method for the synthesis of bimetallic Copper-Silver nanoparticles with simple and cheap laboratory equipments under normal conditions.

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