

A Comparative Review on the Synthesis, Stabilization, and Applications of Silver and Copper Nanoparticles

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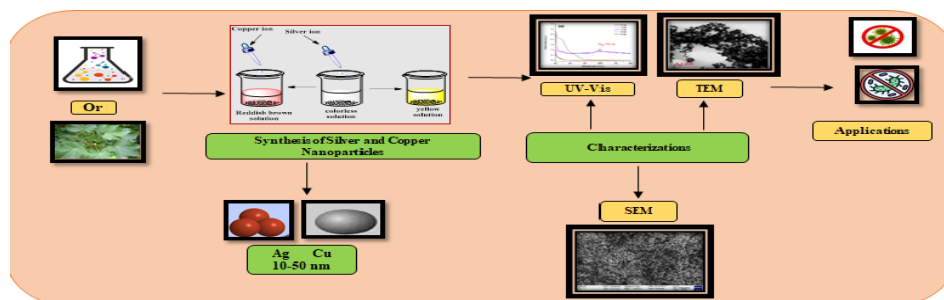
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Abstract

Metal nanoparticles (MNPS) with unique and size-related optical properties that differ greatly from those at the bulk and atomic levels are included in the broad area of nanoscience. Silver nanoparticles (AgNPs) one of the noble MNPS, have special characteristics for metal interaction. Copper (Cu) and silver (Ag) Nanoparticles can be synthesized by using different methods, including chemical, physical, biological and green synthesis techniques. The synthesis of nanoparticles through the use of plants represents biological method that is both environmentally friendly and cost-effective. We produce two types of nanoparticles: one being silver nanoparticles (Ag-NPs) and the other copper nanoparticles (Cu-NPs). The chemical methods of nanoparticles synthesis pose health hazards and environmental risks; the biological method of nanoparticles synthesis is significantly more environmentally friendly and safe for use. Green synthesis, which involves the use of plant extract, bacteria and fungi an eco-friendly approach to nanoparticles production. Controlling the particle size – dependent properties of these nanoparticles enhance their potential application. While silver and gold nanoparticles are widely studied, copper nanoparticles present a cost-effective alternative with strong antibacterial properties. This review compiles information on the synthesis, properties, stabilizing agent, application of Ag and Cu nanoparticles, their importance in biological and technological fields. Characterization by UV-Vis spectroscopy, Fourier-transform infrared Spectroscopy (FTIR), Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), Dynamic light scattering (DLS), etc. copper nanoparticles generally display a surface Plasmon resonance (SPR) peak within the range of 300-800 nm, with notable peaks occurring around 540-570 nm. Silver nanoparticles usually present a peak within the range of 390-470 nm.

Keywords: Silver nanoparticles, Copper nanoparticles, UV-Vis, TEM, SEM

Graphical Abstract



The TEM micrograph and SEM micrograph shown in the graphical abstract are adapted from reference [43], whereas the UV-Vis absorption spectrum image is adapted from reference [42].

Introduction

The simplest type of structure with a diameter under 100nm is known as an NPs, and it demonstrated unique feature that are scale-dependent [1]. Due to their distinctive optical qualities, silver and gold nanoparticles were originally utilized to make stunning stained glass window around 2000 B. C. this is the earliest known instance of nanotechnology. A variety of painted glasses by combining Nano-gold and silver solution [2]. NPs are being utilized as treat cancer [3] to catalyst different reaction⁴, chemical and biological sensor[5]. NPs are collections of several hundred to several millions atoms or molecules. They could have made up of two or more distinct species, identical molecules or atoms, or both. The word Nano is derived from the Greek word Nano’s, means draft or extremely small. Now a days Nano is denoted 10⁻⁹m in S.I. units. The word nanoscience denotes the study of manipulation and engineering of materials, particles and system in the 0.1 to 100 nm.

It entails the comprehension and developing of new methods for the synthesis of nano materials (NMs), whose characteristics are greatly enhanced and distinct from those of bulk materials [6]. e.g., nanoscale gold can have different electrical, optical, mechanical properties to that of its bulk scale. The term “nanotechnology” relates to the application of nanoscience to the creation of practical goods using novel nanoscale materials and components.

Custom-made nanomaterials (NMs) and products with new, improves features will eventually be utilized in a various of field, like Nano electronics components, drugs, sensors, textile industries, and biotechnology, to bring superior technologies to society. Metal nanoparticles (NPs) have been regularly employed in dyeing fabrics, coloring spectacles, and other decorative purpose since mediaeval times and the time of the ancient Romans[7]. The Lycurgus cup is an another man made example of the Roman times in Fourth Century A.D., which is Currently in the British Museum, show unusual optical effect. The glass appears in two different color i.e., deep red in transmitted light and green in reflected light as show in Fig. 1[8] The chemical analysis of this glass revealed that the unusual color change is because the Surface Plasmon Resonance of Nano size Au and Ag where Cu NPs were re-dispersed throughout the glassy matrix.

This discloses in what way the people in ancient times used colloidal Au and Ag NPs to succeed the color-shifting effect [8].



Fig.1 the Lycurgus cup in both transmitted (right) and reflected (left) light Reference. [8]

Synthesis of Silver and Copper Nanoparticles

There have been three different methods used to create nanoparticles, including physical, chemical, and biological processes. Water or organic solvents are used in chemical processes to create silver nanoparticles. Three primary ingredients are often used in this process: stabilizing/capping agents, reducing agents, and metal precursors.

There is numerous synthesis methods for preparation of NPs inclusive of physical and chemical methods. The synthesis techniques typically follow two methods, ‘top-down’ and ‘bottom-up’ strategies. In the method Top-down nanoparticles is created from big materials that are broken up into the required shape and size particles using a variety of approaches. In top down approach various types of physical methods are [a] Ball milling, [b] Electrodeposition, [c] Laser ablation, [d] Aerosol synthesis, [e] Plasma synthesis, [f] Inert gas condensation, [g] Chemical vapor deposition, etc., which have implemented for the successfully produce of NPs in a diversity of environment. In the bottom-up method, NPs are synthesized from atom or molecules. With this method, the NPs that are produced have fewer defects, a more uniform chemical composition, and better long and short range ordering. There are numerous chemical techniques or bottom-up approaches to obtain NPs, including (i) chemical reduction, (ii) photochemical, (iii) hydrothermal/solvothermal, (iv) sonochemical, (v) electrochemical, (vi) micro emulsion, (x) sol-gel, (xi) co-precipitation, etc. [9] Fig.2. [10]

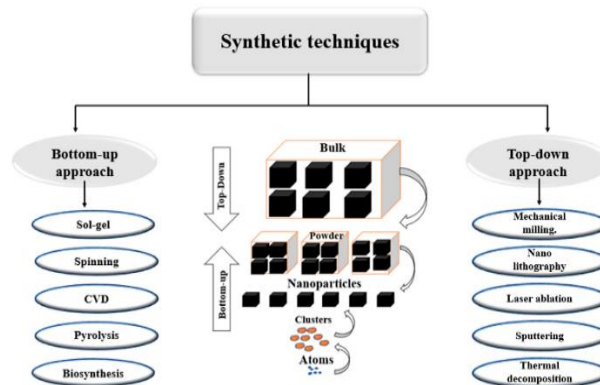


Fig. 2 Metal nanoparticle synthesis using Top-down and Bottom-up approaches Reference. [10]

Nanoparticles based on Silver (Ag), Gold (Au), Copper (Cu), Iron (Fe), Zinc (Zn), Platinum (Pt) and other metals are highly regarded in drug. Faraday [1857] demonstrated the existence of metal NPs in solutions. Researchers looked at the form and color of metallic nanoparticles (NPs) [6]. Presently, NPs can be created and changed by altering their chemical groups, which improves antibody binding. Numerous biological applications, including Anticancer, Radiotherapy enhancement, Drug delivery, Thermal, Ablation, Antibacterial, Diagnostics assays, Antifungal, gene delivery and many more, utilize Nobel metal nanoparticles (NPs), which include silver, gold, and platinum[11]. The unique characteristics of the precious metal NPs improve its value.

Metal NPS can be functionalized with a various of functional groups, like as peptides, antibodies, Ribonucleic acid (RNA) Deoxyribonucleic acid (DNA) to target various cell along with potential biocompatible polymers, like polyethylene glycol. AgNPs are among the most alluring inorganic materials because of its environmental free nature [12]. Additionally, it has several applications in numerous fields like in photography, diagnostics [13], up catalysis, biosensor and antimicrobial. From the pioneering studies; it is now well known that citrate acted in both directions. First is to stabilize the

nanoparticles and to reduce the metal cation. This reactant was extremely important in determining the particle development. For the most part gold (Au), and copper (Cu) have been utilized to create stable dispersions of NPs, which have applications in Surface-Enhanced Raman Scattering [SERS] detection, photonics, catalysis, biological labelling, photography, and photonics.

In general, both physical and chemical procedures can be utilized to prepare and stabilize metal nanoparticles; the chemical techniques, which include Chemical Reduction, Electrochemical approaches, Photochemical reduction is the most popular [14]. It is well known that silver (Ag) acts as a catalyst in the oxidation of Methanol (CH₃OH) to Formaldehyde (CH₂O) and Ethylene to Ethylene oxide [15]. The most popular techniques for creating stable, colloidal dispersions of silver nanoparticles in water or organic solvent in chemical reaction.

The reduction of silver ions (Ag⁺) in aqueous solution colloidal silver with particles diameters measuring several nanometers typically produces [16]. Ions are reduced in various complexes. The synthesis of NPs requires the use of metal precursor, reducer, and stabilizing agent [6]. The most frequently used precursor to produce Nano silver is silver nitrate (AgNO₃) [17]. Various reductants are used, including elements hydrogen, NaBH₄, and organic compound like Alcohol (C₂H₆O) and phenol (C₆H₅OH). These compound function not only as reductants but also as solvent and stabilizing agent during the nanoparticles synthesis process. Aldehyde, Alkoxides, Organic acids, Formic acid, Ascorbic acid, Citric acid and are widely utilize as reducing agents in NPs synthesis. Nitrogen-containing compound like, Hydrazine, Hydroxylamine, Amines are common use.[18-23]

The agglomeration of nanoparticles (NPs) is prevented by employing different stabilizers [stabilizing agent]. Compound like the glucose ethylene glycol, ethanol, sodium citrate, hydrazine hydrate, polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) are known to be effective stabilizers and also function as reducing agent. Stabilizer and surfactants containing functional group, especially Amines, Hydroxyl, Carboxylic acid, Thiols, serve as effective capping agent [24]. Silver nanoparticles (AgNPs) once synthesized, are characterized using a wide range of instruments. In addition to analyzing the size and shape, it is also essential to evaluate other factors like the Size distribution, Surface charge, Surface area. [25]

The most commonly used techniques include UV-Visible Spectroscopy, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transformer Infrared Spectroscopy (FTIR), Dynamic Light Scattering (DLS), Zeta Potential and Nuclear Magnetic Resonance (NMR). [26,27]

Swati Raina et al, have synthesized silver and copper nanoparticles were created by *Centella asiatica* green leaves, cupric sulphate, silver nitrate is used. After adding of plant extract the color changed from colorless to bluish-green, indicating the synthesis of copper nanoparticles. While the creation of yellowish-brown coloration indicated the synthesis of silver nanoparticles.

The absorption spectra of silver nanoparticles were recorded in the range of 300-700 nm, whereas copper nanoparticles were analyzed in the range of 200-700 nm. The morphology and shape of the synthesized nanoparticles were examined using scanning electron microscopy (SEM). [28]

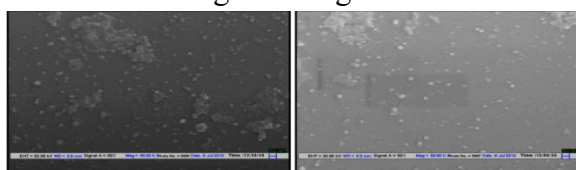


Fig. 3 SEM image of Silver and Copper nanoparticles [28]

Silver nanoparticles with tri-sodium citrate and sodium borohydride as a stabilizing agents and AgNO_3 as a precursor. Sodium borohydride work as a reducing agent when synthesis of silver nanoparticle having a size rang 5 to 20 nm.

The characterization was performed using scanning electron microscopy (SEM), Transmission Electron Microscopy (TEM), Dynamic Light Scattering (DLS), and Ultraviolet –visible spectroscopy. The study of Dynamic Light Scattering (DLS) utilizes two methods: general purpose mode and multiple narrow mode. [29]

Mihir Mehta et al, the method describe Chitosan copper nanoparticles were created by reducing three various copper salts, copper acetate, copper chloride, copper sulphate pentahydrate, chitosan is used. The reducing agents in this case are sodium hydroxide and ascorbic acid. When we addition of NaOH, in 15 minute the color of copper acetate, copper chloride and copper sulphate changes from blue to dark blue, then brown and finally dark brown. When ascorbic acid (AA) was added, the color of the copper chloride solution became colorless. The color changed to milky white and progressively transformed over the next 12 hours into yellow, orange, brown and ultimately dark brown. Upon the addition of ascorbic acid (AA), the blue of copper acetate and copper sulphate shifted from blue to dark blue and then gradually transitioned to orange brown and ultimately dark brown. As synthesized and capped copper nanoparticles are characterized by [UV-Vis] UV-Visible spectroscopy with spectrum obtained broad peaks were visible in the CCNPs synthesized by NaOH around 500 to 600 nm. FTIR result indicated the presence of C=C, C-O, hydroxyl, Oxidized ester carbonyl, conjugated carbonyl and polyhydroxyl group were accounted for stabilization of CCNPs.

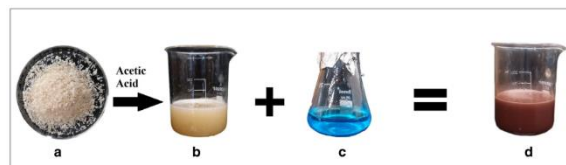


Fig.4 Image of Chitosan copper nanoparticles Reference. [30]

Ascorbic acid and sodium hydroxide are both reducing agent. The utilized copper salt and reducing agents affected the shape, size and crystallinity of the CuNPs. The strong antimicrobial activity against gram - positive bacteria, gram - negative bacteria showed a greater zone of growth inhibition. The FE-SEM result showed that the type of copper salt and reducing agent utilized affected the size and shape of CCNPs.[30]

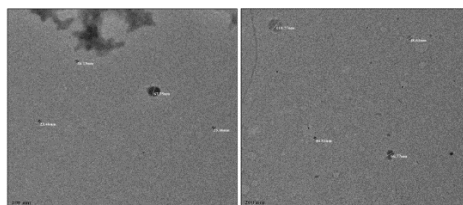


Fig.5 Tem image of Chitosan copper nanoparticle Reference. [30]

F. Laghrib et al, have synthesized chitosan silver nanoparticles were created reduction of silver nitrate (AgNO_3) using sodium borohydride (NaBH_4) and chitosan a s stabilizing agent. To produce a homogeneous solution, chitosan was dissolved in acetic acid and stirring overnight. AgNO_3 was added

Pei-jun Li et.al pectin based copper nanoparticles using pectin, ascorbic acid, sodium hydroxide, copper chloride. The solution was brown. The ultraviolet spectrum peak at 592 nm. Absorbance peak rise with alkali concentration up to 5 g/l and then decrease as seen in figure [43].

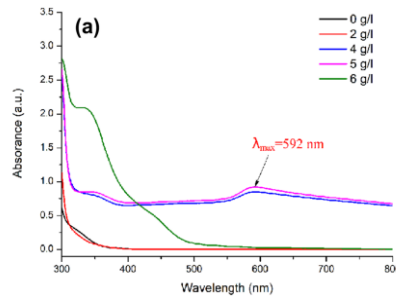


Fig.8 UV-Vis spectra for different ultrasonic frequency Reference. [43]

Deepti Chauhan et.al describe chemical reduction method for synthesizing of copper nanoparticles using chemical reduction method of copper sulfate with sodium hypophosphite, ethylene glycol and using polyvinylpyrrolidone as a stabilizing agent. Techniques most commonly used are; X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques [44].

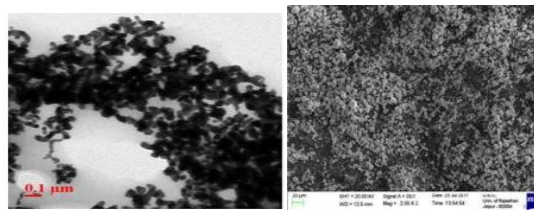


Fig.9 TEM and SEM image of copper nanoparticles Reference. [44]

Manjua Gondwal et al, described the synthesized silver and copper nanoparticles using Cassia Occidentalis leaves, silver nitrate, cupric nitrate, indicating silver nanoparticles color change colorless to yellow and copper nanoparticles color change colorless to bluish green.

The absorption spectra were recorded silver nanoparticles in the range of 300-700 nm and copper nanoparticles were analyzed in the range of 200-800 nm.

Aggregates of Cassia Occidentalis silver nanoparticles with average particles size between 20 and 65 nm and copper nanoparticles with size between 30 and 65 nm are clearly visible in the SEM micrographs.

The TEM micrographs synthesized AgNPs and CuNPs have particle size between 5 and 25 nm and 5 and 30 nm, respectively. [45]

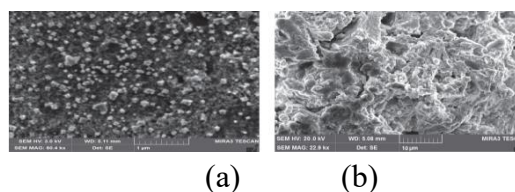


Fig.10 SEM micrographs of synthesized (a) AgNPs (b) CuNPs [45]

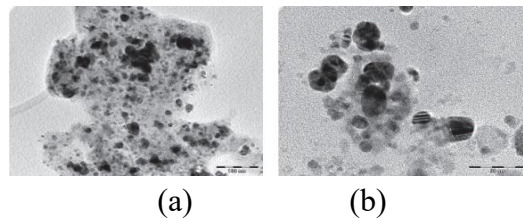


Fig.11 The scale bar in the TEM micrograph of the AgNPs used by *Cassia Occidentalis* corresponds to (a) 100 nm and (b) 50 nm.[45]

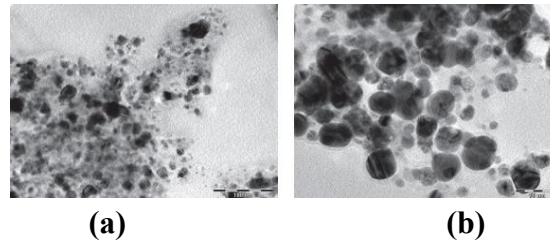


Fig.12 The scale bar in the TEM micrograph of the CuNPs used by *Cassia Occidentalis* corresponds to (a) 100 nm and (b) 50 nm. [45]

The synthesis of nanoparticles mediated by *Ocimum Sanctum* (Tulsi) was validated through UV spectroscopy, which indicated a surface Plasmon resonance (SPR) peak at 400-450 nm. Scanning electron microscopy (SEM) analysis showed that the nanoparticles varied in size from 8 to 140 nm and exhibited a spherical morphology [46].

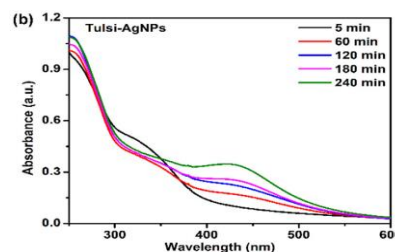


Fig.13 UV-Vis spectra for different ultrasonic frequency Reference. [46]

Application

Various metal nanoparticles with antibacterial properties, including silver, copper and gold nanoparticles, have been area of research. According to studies these nanoparticles exhibit antibacterial action against both Gram-positive and negative bacteria, including *Escherichia coli* and *staphylococcus aureus*. These metal are widely used in sunscreen lotion, dental material, medicine and water treatment. In addition to their antibacterial effect against the aforementioned microorganisms, they also affect *Bacillus subtilis*. Due to their inexpensive cost, copper and silver nanoparticles are frequently compared. Three types of bacteria stood out when comparing the bactericidal effects of silver and copper on different microbiological strains: *E. coli*, *B. Subtilis* and *S. aureus*. There was not a significant difference in the *S. aureus* strains sensitivity to silver and copper nanoparticles. However, it was shown that there is less of sensitivity difference between silver and copper when comparing *E. coli* and *S. aureus*. [47] Using the agar well diffusion method, the antibacterial potential of the synthesized copper from *Kigelia Africana* against a few test pathogens was studied. The diameter of the zones of inhibitions was then

measured in millimeters to determine the antibacterial activity. [48] They also affect The antibacterial spectrum of AgNPs encompasses both organisms are gram-positive and gram-negative. However, different mechanisms for antibacterial action have been notified, the precise mode of action is still unknown [49]. The primary mechanisms of action include the ingestion of free silver ions, which disrupt ATP molecules and inhibit DNA replication, the production of Reactive Oxygen Species (ROS) by silver nanoparticles and the direct damage caused by silver ion (Ag^+) to cell membranes. It is known that Silver nanoparticles increase permeability and lead to cell death by creating pit in the cell walls of gram-negative bacteria.

Consequently, AgNPs usually lead to denaturation and oxidize the cell walls [50]. In addition, Silver nanoparticles (AgNPs) modify the phosphotyrosine profile of peptides, disrupting signal transduction and inhibiting cellular growth [51]. According to monisha singhal et al experiments from 2021 50-60 $\mu\text{g cm}^{-3}$ of AgNPs completely inhibits Escherichia coli bacterial growth [52]. AgNPs' bactericidal abilities are also size-dependent. AgNPs that directly contact with the surface of a cell membrane and are in the range of 1 to 10 nm modify the permeability and harm the cell [53]. The exterior proteins of viruses may connect with AgNPs, preventing the attachment and multiplication of the viruses. Future study is still possible despite the fact that the antiviral mechanism of AgNPs is still not fully understood [54]. 44 isolates of different fungus species were resistant to the antifungal effects of AgNPs [55]. AgNPs' (Silver Nanoparticles) ability to limit cell growth against Candida albinos may be caused by the breakdown of cell membrane integrity [56].

Silver nanoparticles can therefore be one of the treatments used to stop fungal infections of the oral tissues. Silver Nanoparticles incorporated into resins at a concentration of 1 $\mu\text{g/ml}$ have shown potent antifungal activity without cytotoxicity [57]. In many industrial application areas, nanotechnology has helped to sustain competitiveness and growth [58]. Nanoparticles' physical and chemical characteristics serve practical use [9]. That are being quickly utilized in a variety of fields, including those of medical, biotechnology, material science, and energy. In fact, biotechnology uses cellular, molecular, and genetic processes to create medications specifically for agricultural use. Due to their size, distribution, and morphology, innovative uses of nanoparticles and nonmaterial are fast expanding on a variety of fronts [10]. The size & shape of the nanoparticles are utilized to define the characteristic features of the nanostructures, which are frequently used in nanotechnology applications. For a number of reasons, the demand for nanoparticles is increasing due in many industrial application areas, nanotechnology has helped to sustain competitiveness and growth to their economical and environmentally friendly synthesis. The antibacterial activity, it is exciting to synthesize nanoparticles utilizing physical and chemical approaches that bring dangerous and harmful elements into the system [59]. Chemical, and biological properties However, biological rather than chemical or physical ways of extracting plants proves to be more successful. This s due to the facts that physicochemical approaches do not fit the size and shape of nanoparticles produces by the physical and chemical procedures. New the disease caused by the body like an Avian influenza, HIV/AIDS, the middle east respiratory syndrome (MERS) Ebola virus, zica virus and others are being exposed on a daily basis, making treatment of these new diseases difficult. Researcher are focusing on using AgNPs as a treatment for various illnesses because of their distinct physical, chemical, and biological properties [60]. Synthesis of nanoparticles utilizing biological processes, as an alternative to both chemical and physical approaches, like those involving microorganisms [61], enzymes, fungus and plant extract, [62,63] has been presented as a potential

environmental friend. [64] The synthesis of plant extract for green and silver nanoparticles are cost-effective, easy and environmentally beneficial technology.

The probability can be eliminated by synthesizing silver nanoparticles. When it comes to chemical stability and catalytically activity for antibacterial, [65] antivirals, anticancer, antifungal, and anti-inflammatory [66] characteristics, silver nanoparticles are superior to other metallic nanoparticles. [67] difference in cell structure, physiology, metabolism, or the extent to which organisms come into contact with nanoparticles could be the cause of variations in the sensitivity or resistance of populations of both Gram-positive and negative bacteria. Because of electrostatic force, and bioactivity are thought to be caused by the opposing charges of bacteria and copper ions produced from nanoparticles. Peptidoglycans bind Cu^{2+} ions produced from copper NPs in the liquid growth media because they are negatively charged molecules. The bacterium *E. coli* may let more Cu^{2+} ions to enter the plasma membrane due to its Gram-negative status, although it is generally thought to be less dependent on antibiotics and antibacterial treatments than Gram-positive bacteria. Ultimately it may be said that Gram-negative bacterial strains exhibit greater antimicrobial activity than Gram-positive strains due to their membrane shape. [68]

Conclusion

Metal Nanoparticles are important in both nanoscience and Nano technology. Silver and copper nanoparticles can be synthesized utilize both top-down (Physical) and bottom-up approaches. Physical approaches typically involve expensive equipment, high temperature and vacuums, making this method uneconomical. The least harmful and most environmentally friendly techniques were discovered to be in a biological nature. The synthesized nanoparticles can be examined through a range of analytical methods, including assessment of their shape, size Functional group, structure and characterized.

Although biological techniques are also utilized to create copper nanoparticles, they are not appropriate for our situation due to a lack of understanding and expensive with the techniques. Chemical techniques can be created using basic laboratory equipment under ambient conditions and are extremely straightforward, versatile, affordable, provide high yields, and are environmentally benign. These methods allow us to create homogeneous, widely distributed, and tunable nanoparticles in terms of size and shape. After researching chemical technique for producing copper nanoparticles, we discovered that the chemical reduction method is the most efficient. It has been discovered that nanoparticles (NPs) are crucial to the pharmacological, biological and medicinal uses of nanotechnology.

Additionally, there are a variety of methods to make copper nanoparticles through the chemical reduction method. Few scientists utilize inert media to prevent oxidation and various hazardous and costly compounds as reducing and capping agents, which increase the cost and hazard of production. Researcher on chemical reduction techniques showed that, with the exception of ascorbic acid, all reducing and capping agents/chemicals are very costly and hazardous. Since ascorbic acid (Vitamin C) is nontoxic, affordable and has both reducing and protective properties, we chose it for our synthesis procedure.

Abbreviations

Cu – Copper

Ag – Silver

MNPS - Metal nanoparticles

AgNPs - Silver nanoparticles
CuNPs - copper nanoparticles
UV-Vis- Ultraviolet –Visible spectroscopy
FTIR- Fourier-transform infrared Spectroscopy
TEM - Transmission electron microscopy
SEM - Scanning Electron Microscopy
DLS- Dynamic light scattering
SPR - Surface Plasmon resonance
NPS- Nanoparticles
NMs - Nanomaterials
Au – Gold
Zn - Zinc
Fe – Iron
Pt – Platinum
RNA- Ribonucleic acid
DNA- Deoxyribonucleic acid
SERS- Surface-Enhanced Raman Scattering
AgNO₃ - Silver nitrate
PVA - Polyvinyl alcohol
PVP - Polyvinyl pyrrolidone
XRD - X-Ray Diffraction
NMR - Nuclear Resonance
HH- Hydrazine hydrate
NMR - Nuclear Magnetic Resonance
SFS - Sodium formaldehyde sulfoxylate
AA- Ascorbic acid
CCNPs - Chitosan copper nanoparticles

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