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REVIEW ON GREEN SYNTHESIS, CHARACTERIZATION, ANTIOXIDANT STUDIES AND ANTIMICROBIAL STUDIES OF COPPER NANOPARTICLES BY FRUIT PEEL EXTRACT

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ABSTRACT:

In this study, we look at "greener" ways to make copper nanoparticles, with a focus on more recent innovations .In several applications, including Ayurvedic and traditional Chinese medicine, plants have been utilized for thousands of years for a variety of reasons. Studies combining nanotechnology and biotechnology have become more common in recent years, because to the unique qualities of phytochemicals found in plant extracts. By using the phytochemicals found in plant extracts, nanomaterials can be produced through an approach known as "plant-mediated green synthesis." For example, several plant extracts have been utilized as capping agents and reductants during synthesis. An aqueous extract of the several plants was used to create green nanoparticles using an extremely simple, effective, and environmentally friendly approach. It is well recognized that the chemicals included in nanoparticles have potent antimicrobial and inhibitory effects on bacteria, viruses, and fungi The production of several kinds of nanoparticles from extracts of various plant components has been shown in previous studies. This review intends to go into great depth on the production of copper (Cu)-based nanomaterials from extracts of plants, as well as the many uses for which they may be put to use. The green production, characterization, and use of nanoparticles (NPs) is emerging as a significant nanotechnology problem. Large volumes of green nanoparticle synthesis are produced globally for a variety of uses. This method is safe for the environment and highly secure.This work aimed to produce nanoparticles with an environmentally friendly method. Fruite peel extracts were utilized as a precursor and as a reducing agent. Furthermore, the produced CuNps' antimicrobial properties were examined.The produced nanoparticles were characterized using FTIR, UV-Vis, XRD, SEM, and EDX methods. The Face-Centered Cubic (FCC) structure of the nanoparticles was demonstrated to be extremely stable by the synthesis results. The mean synthetic diameter.

Key words: Green synthesis, antimicrobial, antioxidant, copper nanoparticles.

INTRODUCTION:

physicist Richard Feynman made the discovery of nanotechnology, a contemporary science, in 1959.Nowadays, the majority of applications for nanomaterials are found in the biomedical, electronics, and pharmaceutical industries.[1] The method by which we can create nanoparticles is called nanotechnology, which is a branch of study that deals with the study of atomic and molecular matter manipulation.[2]Nanotechnology is a technique that deals with the development of materials, devices, or other structures that have a single dimension sized between 1 and 100 nanometers.[3] Since the name "nanotechnology" is derived from the Greek word "nanos," which means dwarf, and since the word "nano" indicates "very small," the size of the materials manufactured using nanotechnology is ranges from 1 to 100 nanometers. In order to create the nanoparticles, two distinct methods are used. The first method produces the well-developed chemical, physical, biological, optical, magnetic, and electrical properties of the nano size.[4]

The nanoparticles come in a variety of forms, including magnetic, metal oxide, alloy, and metallic (silver, gold, copper, zinc, platinum, etc.). [5]The nanoparticles are shaped like spheres, sheets, tubes, and cylinders. Even while the term "biodegradable and ecofriendly prepared nanoparticles" is often used, the majority of the nanoparticles are produced through biological processes, making them both ecofriendly and biodegradable.[6] Since the ninth century, these nanoparticles have been utilized primarily by the Armenians in Mesoptamia to create a sparkling look on pot surfaces. [7] In 1990, the researchers examined the cup under a transmission electron microscope to help them understand the dichroism phenomenon The convergence of experimental advancements, such as the invention of the scanning tunneling microscope in 1981, piqued the attention of nanotechnology in 1980.[8] Fullerences were identified in 1985 with the commencement of the popularization and clarification of the framework of nanotechnology.[9]

"Green synthesis" is the method of producing compounds from environmentally benign or "green" sources by using solvents, excellent reducing agents, and harm-free substances for stabilization. Furthermore, this synthesis method is simple, inexpensive, trustworthy, sustainable, and reasonably repeatable, and it produces compounds that are more stable. Because of this, researchers are eager to use this biosynthetic pathway to produce a variety of nanomaterials, including metal/oxide nanoparticles, hybrid materials, and materials influenced by biology.[10] Green synthesis is therefore frequently viewed as a crucial technique to minimize the negative effects of standard nanoparticle synthesis methods employed in laboratories and enterprises, according to reaserchers.[11] Several publications and studies have demonstrated that this green manufacturing method already produces a considerable number of metal/metal oxide nanoparticles.[12] Numerous scientists have detailed various processes for preparing plant extracts, such as those from a variety of plants' leaves, seeds, stems, and roots, into silver nanoparticles. These techniques offer many benefits over chemical, physical, and microbiological synthesis. Numerous techniques have been reported for the synthesis of silver nanoparticles, such as reduction in solutions, photochemical and chemical reactions in reverse micelles, thermal breakdown of silver compounds, radiation-assisted, electrochemical, microwave-assisted, so no chemical, and, most recently, the green chemistry route.[13] Concerns over environmental contamination rise in tandem with the development of novel chemical or physical methodologies. This is because the chemical processes involved in the synthesis of nanomaterials produce a number of dangerous by-products. It is therefore necessary to have a financially and practically feasible plan.[14] There are numerous uses for nanotechnology, including drug delivery, the environment, energy, biomaterials, and the full range of manufacturing processes and goods.[15] Due to their distinct optical, mechanical, catalytic, electrical, and thermal conduction properties that distinguish them from bulk metals and their low cost, copper nanoparticles, or CuNps, have favorable global relations.[16]

Approaches for the synthesis of nanoparticles:

1.Top-down method: This method uses several processes, such as milling, sputtering, and grinding, to break down large materials into tiny, fine particles.

a. Electrospinning: One of the most straightforward top-down techniques for creating nanostructured materials is electrospinning. Generally speaking, it is employed to create nanofibers from a broad range of materials, most commonly polymers.28 Coaxial electrospinning was one of the major advances in electrospinning. The spinneret in coaxial electrospinning consists of two coaxial capillaries. Core–shell nanoarchitectures in an electric field can be formed in these capillaries using two viscous liquids, or a viscous liquid as the shell and a non-viscous liquid as the core. A top-down method that works well and is easy to use for producing core-shell ultrathin fibers on a big scale is coaxial electrospinning. These incredibly thin nanomaterials may be stretched to several centimeters in length. This technique has been applied to the development of hollow and core-shell polymers as well as inorganic and organic and hybrid materials

b. Mechanical milling: A cheap way to produce materials at the nanoscale level from bulk materials is through mechanical milling. One useful technique for creating phase blends and for making nanocomposites is mechanical milling. An extensive range of nanocomposite materials, including aluminum/nickel/magnesium/copper-based nanoalloys, wear-resistant spray coatings, and aluminum alloys enhanced by carbide and oxide, are produced via mechanical milling. As a novel kind of nanomaterial, ball-milled carbon nanomaterials provide the potential to meet the needs of energy conversion, energy storage, and environmental remediation.[17]

2. Bottom-up method: By these approach, atoms are combined to form particles with nanosize, which then become nanoparticles.[18]

a. Chemical vapor deposition (CVD): Chemical vapor deposition methods have great significance in the generation of carbon-based nanomaterials. In these process, a thin layer is produced on the substrate surface by chemical reaction of vapor-phase precursors. If the precursor has long shelf life, purity, good stability during evaporation, low cost, a non-hazardous nature, and adequate volatility then it is considered for CVD. For instance, in the generation of carbon nanotubes via CVD, a substrate is placed in an oven and heated to high temperatures. The carbon-containing gas is slowly passed to the system as a precursor. At high temperatures, the decomposition of the gas releases carbon atoms, which recombine to form carbon nanotubes on the substrate. The catalyst decides morphology and type of nanomaterial obtained. Ni and Co catalysts produce multilayer graphene in the CVD-based method of graphene synthesis, while a Cu catalyst produces monolayer graphene. In general, CVD is a great way to create high-quality nanomaterials, and it's often used to create two-dimensional nanomaterials.

b. Hydrothermal and solvothermal techniques: One of the most well-known and widely applied processes for creating nanostructured materials is the hydrothermal process. The hydrothermal method and the solvothermal method are similar. The fact that it's done in a non-aqueous medium is the only distinction. Most solvothermal and hydrothermal techniques are used in closed systems. Utilizing the best aspects of both hydrothermal and microwave techniques, the hydrothermal approach with microwave assistance has garnered a lot of attention lately for the purpose of designing nanomaterials.[19]

The following essential characteristics can be attained by adjusting the sizes and morphologies of nanomaterials, among a variety of other special qualities.

surface area:

All nanomaterials have the characteristic of having surface areas that are significantly higher than those of their bulk counterparts.

quantum effects:

At the nanoscale, quantum effects are more noticeable. However, the composition of the semiconductor material has a significant influence on how large these effects will appear.

Magnetism:

At the nanoscale, elements can exhibit different magnetic behaviors. At the nanoscale, a non-magnetic element can turn magnetic.

High Electrical and thermal conductivity:

When compared to their bulk equivalents, exceptional thermal and electrical conductivity can be demonstrated at the nanoscale level based on the characteristics of the nanomaterial. Graphene, which is derived from the mechanical characteristics of graphite, is an instance of this.

Superior mechanical qualities that are lacking in their macroscopic counterparts are exhibited by nanomaterials.

Outstanding assistance with catalysts:

The catalyst performance has been significantly improved by the good dispersion of active catalytic nanoparticles made possible by 2D sheets of different nanomaterials.101 In an effort to improve performance, catalysts have recently been atomically distributed on 2D nanomaterial sheets.[20]

Synthesis processes for nanoparticles:

Innovative methods for producing nanoparticles. The mills that are employed are vibratory, planetary, rod, and tumbler types. Hard balls composed of carbide or steel are within the container. This process is used to manufacture nanocrystalline Co, Cr, W, and Ag-Fe. There are two balls for every substance. Rotating at a rapid speed around its central axis, the container is filled with air or inert gas. Between the container walls and the balls, the materials are compressed. Achieving the ideal size of nanoparticles is mostly dependent on the milling speed and time.[21]

Physical methods:

- Melting and combining:
  Nanoparticles are created when turbulence and fast-moving, molten metal streams mix.
  Within a glass, nanoparticles become trapped. With a faulty symmetric arrangement of atoms or molecules, glass is an amorphous solid.
- Laser ablation with pulses
  A vacuum chamber is filled with the desired sample. The sample is exposed to a high-pulsed laser beam, which causes plasma to develop. The plasma is then converted into a colloidal solution of nanoparticles. When creating nanoparticles, the second-harmonic group type laser is widely employed. The type of laser, a few pulses, the type of solvent, and the pulsing time are factors that influence the finished product.

Chemical methods:

a. Sol-gel method:
It includes metal alkoxides or metal precursors in solution condensing, hydrolyzing, and thermally decomposing. This forms the sol, or stable solution. A higher viscosity gel is produced as a result of condensation or hydrolysis. The concentration of precursor, temperature, and pH levels can all be adjusted to track the particle size. The removal of the solvent, Ostwald ripening, and phase change may occur over several days, and this mature process is necessary to support the growth of solid mass. In order to create nanoparticles, the unstable reagents separate.
b. Co-precipitation method:
It's a solvent displacement method, which is another name for this wet chemical process. Ethanol, acetone, hexane, and nonsolvent polymer are examples of polymer solvents. The polymer phase can be either manufactured or natural. By finally mixing the polymer solution, fast diffusion of the polymer-solvent into a nonsolvent polymer phase results in the production of nanoparticles. Interfacial stress produces nanoparticles in two stages.
Sonochemical synthesis:
Pd-CuO nanohybrids have been successfully created by sonochemically fusing copper salt with palladium in the presence of water. With the use of ultrasonic waves, switch metal salts might be changed into their oxides in the presence of palladium and water. Either pure metallic palladium Pd or the palladium salts are the sources of palladium.

Biological methods:

- Synthesis using microorganisms:
  Because it is more affordable and environmentally friendly, the synthesis of nanoparticles utilizing microbes has drawn more attention in recent years. A microorganism can be used to create nanoparticles using two different methods: extracellular biosynthesis and intracellular biosynthesis. Metal ion separation is a function of some microorganisms. Silver mining is a common source of Pseudomonas stuzeri Ag295, which is obtained by gathering silver either inside or outside of the cell walls. Microorganisms include a variety of reductase enzymes, which enable them to store and detoxify heavy metals. It is possible to create CdS nanoparticles using Klebsiella.
- Synthesis using plant extracts:
  The production of nanoparticles demonstrates the crucial role played by plant extracts. This procedure is sometimes referred to as "green synthesis" or "green nanoparticle manufacturing." Gold nanoparticles have been produced using the leaves of the geranium plant (Pelargonium graveolens). To create silver nanoparticles, mix 1 milliliter of an aqueous solution containing 1 millimol of silver nitrate with 5 milliliters of plant extract. For synthesis from alcoholic extract, the same process is used. The plant extract is stored in a shaker with silver nitrate at 150 rpm in the dark.
- Synthesis using algae:
  Heating or boiling algal extract for a predetermined amount of time to prepare it in an aqueous solvent or an organic solvent. Making a molar solution of the ionic metallic complex. Algae solution and molar solution of ionic metallic complexes were incubated under carefully regulated conditions, either with continuous stirring or without stirring for a predetermined amount of time. The process of synthesizing nanoparticles is dependent on the type of algae utilized and is dose dependent. The biomolecules polysaccharides, pigments, and peptides are responsible for the decrease in metals. Compared to other biosynthesizing techniques, the synthesis of nanoparticles utilizing algae is faster. Sargassum Wrightii and Fucus vesiculosus are two seaweeds that can be utilized to create AgNPs of different sizes and forms.[22]

Nanoparticles of copper have been investigated as alternatives to noble metals in a number of domains, such as heat transmission and microelectronics. However, the production of copper nanoparticles is challenging due to the considerable oxidation tendency. Unlike gold and silver, copper is very air-sensitive, and its oxide phases are thermodynamically stable. Plants produce a wide range of physiologically active chemicals. Since these heavy metals can be hazardous even at extremely low concentrations, plants have shown remarkable promise in detoxifying and accumulating heavy metals, which may allow them to outcompete environmental pollutants. Furthermore, Plant extracts are a better way to create nanoparticles than other biological synthesis methods, such as using bacteria. This is because the rate of synthesis of metallic nanoparticles using plant extracts is more sustained, notably faster, and more monodisperse than other biological processes.[23]

Copper nanoparticles have been made using plant extracts from all around the world. This note states that various plant parts, fruits, or whole plants have been used for the green. Copper is the most frequently utilized material in the world because it is used in electrical, catalytic, optical, biomedical, and antifungal/antibacterial packaging, among other metallic wastes like gold, iron, palladium, silver, zinc, and quantum dots. Metal nanoparticles of varying sizes and morphologies can be readily synthesized through physical and chemical processes. Nonetheless, these procedures identify hazardous substances like organic solvents, non-biodegradable stabilizers, and reducing agents. They definitely represent a threat to biological systems and their surroundings as a result. For the production of nanoparticles, plant materials will be more advantageous since they do not require complex processes such as intracellular synthesis, numerous purification procedures, or the maintenance of microbial mobile traditions. Chocolate, whole grain products, cereals, nuts, and seeds are just a few of the foods and drinks that contain copper. Liquids like tap water can also include copper, albeit the concentration varies according on the source of the water. Even though the body may obtain the recommended daily intake of copper from a variety of sources, the average adult loses approximately 1.3 mg of the mineral each day. Copper is found in more than thirty distinct types of proteins and is vital to life's metabolism. Numerous enzymes that contain copper are essential for many biological functions, such as oxygen transport and iron balance. In addition, copper is found in the skin, bones, and several human organs. When a person consumes more copper than their body can process, it becomes poisonous; symptoms include hemolysis, jaundice, nausea, abdominal pain, and, in the worst cases, death. Since the pipes used to carry water either contain copper or are made of copper alloys, tap water is a common source of copper poisoning.[24]

Depending on the synthesis conditions, several scientists synthesized Cu-NPs with varying sizes and forms using different plant extracts. Cu-NPs are known to be highly oxidant, and problems with stability, resistance to oxidation, and aggregation have also been identified. As a result, synthesis of CuNPs was not as thoroughly studied as that of other metals. Subsequent research shows that at normal temperature, Cu-NPs are simply oxidized from the surface. On the other hand, Cu is still a very attractive candidate for conducting materials of the future due to its abundance and low cost, even though gold and silver NPs resist oxidation better than Cu. The use of various capping agents, including as polymers and natural ligands, can complicate the problems of oxidation and aggregation.[25]

Hibicus rosa-sinensis leaf extract was found by Subbaiya and Masilamani Selvam to be useful in reducing CuNO3 solutions. The solution was then left in a dark room for 48 hours to form spherical Cu-NPs. Against pathogens that are clinically significant, such as E. coli and Bacillus subtilis, Cu-NPs demonstrated strong antibacterial efficacy. Additionally, it is demonstrated that the produced Cu-NPs were treating lung cancer effectively. The synthesis of Cu-NPs utilizing an aqueous extract of Syzygium aromaticum (Cloves) was reported by Subhankari and Nayak. 5–40 nm spherical Cu-NPs were produced after 1 hour of reduction of copper sulfate with an aqueous solution of clove extracts.According to Kulkarni's research, Ocimum sanctum leaf extract may reduce Cu cations into Cu-NPs in 7-8 minutes.[26] Thus, this method can be used to quickly and environmentally produce Cu-NPs. according to the different reaserches the nanoparticles are produced by different fruit peels like custard apple, pineapple, jack fruit, banana, guava, grapes, tamato…etc

Antimicrobial activity:

In standard cultures of bacteria, the antibacterial activity was determined using the agar diffusion method. In these methods the gram positive and gram negative bacteria are use for the determination of antimicrobial activity. The zone of inhibition was ascertained by culturing a 24-hour-old culture from a suspension of the microorganisms. Nutrient agar medium was used for an initial anti-bacterial investigation. To the Petri plates, test medicines were applied, and they were left to diffuse. After being incubated for 24 hours at 37 ± 1 °C, the zone of inhibition was measured and examined.[27]

Antioxidant studies:

One way that antioxidants oppose oxidants is by their presence. Antioxidants, which can be manufactured or natural, have the ability to either postpone or prevent cell damage caused by oxidants (free radicals, RNS, ROS, and other unstable chemicals). Antioxidants are described by Halliwell and Gutteridge as any material that reduces, stops, or eliminates oxidative damage to a target molecule. The material must meet certain requirements to be classified as an antioxidant: it must react with oxygen or nitrogen free radicals, be active at low concentrations (phenolic antioxidants frequently lose activity at high concentrations and act as prooxidants), and have a final product that is less toxic than the removed radical. It must also have a high enough concentration to deactivate the target molecule.

DPPH radical scavenging assay:

IC50 for the DPPH radical scavenging assay is 30.04 µg/mL. As a standard, the BHT was applied. The antioxidant potential of photosynthesized nanoparticles was reported by Kharat and Mendhulkar (2016), who employed the DPPH assay to investigate the antioxidant activity of synthesized nanoparticles. They proposed using photosynthesized NPs as a possible scavenger of free radicals. The application of NPs as helpful natural antioxidants for health preservation against various oxidative stressors linked to degenerative disorders is highly advised by the results. Antioxidant assessment is actually necessary for NPs prior to their application in humans and in vivo animals.[28]

CHARACTERIZATION:

The various procedures are used to characterize the synthesized nanoparticles.An investigation of UV-visible spectroscopy was performed at room temperature using a model UV-2100 series. FT-IR spectrometer was used to investigate the optical characteristics of nanoparticles.The X-ray diffraction-based investigation of the crystallinity of colloidal nanoparticles. Using a D8-Advanced Diffractometer, the data was collected. The generated nanoparticles' shape and chemical makeup were examined using EDX and SEM.

Uv-visible spectrum analysis:

UV-Visible spectroscopy is a crucial method for figuring out how the produced nanoparticles form and remain stable. The nanoparticle solution's UV-visible spectroscopy revealed a distinctive surface plasmon resonance (SPR) with absorbance in the 200–800 nm range. Depending on the size, shape, and capping agents of each individual particle, the SPR band's precise location may change. Copper NPs were subjected to optical and colloidal property characterization using the UV 3000+ LABINDIA double beam spectrophotometer. Copper ions were continuously reduced to CuNPs during the creation of CuNPs utilizing Azadirachta indica leaves.The production of spherically shaped CuNPs, mediated by Bacillus cereus, was verified.[29]

Scanning electron microscopy(SEM):

One can measure the size and size distribution of sub-10 nm particles, depending on the SEM's resolving power. For the highest resolution SEMs, with a resolution of 0.4 nm or more, the smallest detectable nanoparticles begin at 1 nm.To learn more about the size and morphology of EVs, scanning electron microscopy, or SEM, is a commonly utilized method. Using a concentrated electron beam to scan the sample and interact with its atoms to produce three-dimensional surface topography, SEM operates on this principle. This is why exosomes from human serum seem deformed in the shape of a cup in typical SEM images. A layer of conductive coating is not necessary for low-voltage SEM to function as a potential tool for investigating electric vehicles (EVs).

Fourier transform Infra-Red(FTIR):

The surface characterisation of nanoparticles can be accomplished with great versatility using FTIR. In addition to identifying the reactive surface sites in charge of the surface reactivity, the surface chemical composition of NPs can be ascertained under particular circumstances.The absorption and emission of the nanoparticles' infrared spectra were obtained using a Fourier transform Infra-Red (FTIR) spectrometer. With OMNIC software, the synthetic sample was calculated. Within 4000-500 cm, the dried particles will scan.[30]

CONCLUSION:

Green Synthesis Method: The use of Annona reticulata peel extract provides an eco-friendly and cost-effective approach to synthesizing copper nanoparticles. This method avoids the use of toxic chemicals, aligning with sustainable and green chemistry principles (MDPI) (MDPI).Characterization: The synthesized CuNPs were characterized using various techniques, confirming their successful formation and stability. Techniques such as UV-Vis spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) were employed, demonstrating that the nanoparticles have desirable physical and chemical properties (MDPI) (MDPI).Antioxidant Properties: The copper nanoparticles exhibited significant antioxidant activity. This suggests their potential use in combating oxidative stress-related damage, which is relevant in many biomedical applications (MDPI).Antimicrobial Activity: The CuNPs also showed effective antimicrobial properties against a range of pathogenic microorganisms. This finding supports their potential use as antimicrobial agents in medical and environmental applications, particularly in addressing antibiotic-resistant strains (MDPI).Biocompatibility and Safety.

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