GREEN SYNTHESIS, MORPHOLOGY AND ANTIMICROBIAL ACTIVITY OF COPPER NANOPARTICLES, A REVIEW

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Abstract **:** Copper nanoparticles received much attention due to its high electrical conductivity, high melting point, low electrochemical migration behavior and low cost. This review focuses on the distinct features of synthesis of copper nanoparticles by various methods. A detailed study of reduction of copper ion into copper nanoparticles mediated through chemical and most efficient green synthesis method ware demonstrated with brief experimental procedures. Some method requires external reducing capping and stabilizing agent for synthesis where as other uses radiation source. The synthesize nanoparticles with different size and shapes like cubes, triangular, wires etc. ware characterized through U-V visible spectroscopy, Fourier Transform Infra-Red Spectroscopy, X- Ray Diffraction analysis, Scanning Electron Microscopy(SEM), and high resolution Transmission Electron spectroscopy (TEM). Nanoparticles ware comparatively analyzed for their absorbance, stabilization of bond, particle size in nanometer and particle shapes contributing configuration respectively. The Clinical significance of copper nanoparticles conferring the antimicrobial activity was studied with the zone of inhibition produced by some pathogenic gram positive and gram negative bacteria and fungus respectively. This review emphasis the ecofriendly, cost effective, nonhazardous and green method of synthesis nanoparticles by using different plant part extracts which overcomes the other chemical method with all the way.

Keywords: Green synthesis, Chemical Synthesis, UV visible spectroscopy, SEM analysis, FTIR analysis,

I. Introduction:

The term nanotechnology was define by professor Norio Taniguchi from Tokyo Science university in 1974 as “Nanotechnology mainly consist of the processing of separation, consolidation and deformation of material by one atom or by one molecule” [1]. In recent year nanotechnology attracts many researchers as more than lac of research paper has been published in reputed journals. The nanoparticles refer to the particles of size less than 100 nanometer (nm) [2]. Due to the large surface area properties of nanoparticle alters optical, magnetic, electrical, thermoelectric, optoelectronic, thermomechanical, antibacterial, catalytic properties at Nano level (3-10). It opens the door for interest and wide application of nanoparticles in the field of pharmacy, medicine, industry, biomedical and biofuels as energy production [11-14].

Due to increase in demand by overpopulation causes rapid urbanization and industrialization our environment undergoes great damage by releasing large amount of unwanted and hazardous materials like chemicals and gases [15-16]. Now it is our need to learn about the secrets which are present itself in natures and its products which opens the door of ecofriendly nanoparticle synthesis [17]. The methods used to synthesize Copper nanoparticle by chemical and wide variety of green methods [18-22].

The chemical methods of synthesis of nanoparticle are non-ecofriendly, tedious, expensive, non-handy, require high temperature and toxic chemicals [23 -25]. This needs can be cured by using alternative method of nanoparticle synthesis are green synthesis of nanoparticle by using fungi, yeast, algae, bacteria, and plant parts like leaf, stem, bark, root etc. extract [26-32]. Among these methods some requires the hygienic, closed tissues culture lab [26-27] and these green synthesis of nanoparticles by using the extract of plant parts like leaf, stem, flower, roots are fruitful because of handy, economical, less toxic procedure than the above biological and chemical method of nanoparticle synthesis [26-32]. In the present study, synthesis of copper nanoparticle always a part of interest by the researcher because of Its high electrical conductivity, high melting point, low electrochemical migration behavior and low cost [33].

2.Chemical Method

2.1Chemical Reduction

It is the more common method of synthesis of copper nanoparticles.The reducing agent is added to convert copper (II) to copper (0). Copper nanoparticles are more susceptible for oxidation hence capping and stabilizing agent are added. The organic and inorganic reducing agent played the important role of reducing, capping and stabilizing agent. The Sodium borohydride, Ascorbic acid (C.A), Polyethylene glycol (PEG) Hydrazine, Cetyl Pyridinium Chloride(CPC), Cetyltrimetyl amoniumbromide (CTAB), Diethylenetriamine Rongalite Hydrazine hydrate etc. act as a reducing, capping and stabilizing agent. (34-38) Javier Suarez Cerda and coworker synthesize the copper nanoparticles ascorbic acid as a reducing agent and Cyclodextrin as a stabilizing agent . The size of the copper nanoparticles ranges from 3-33 nm with FCC structure [39]. Thi My Dung dang and coworker synthesized the copper nanoparticles of the size less than 10 nm. The Sodium borohydride act as a reducing, Ascorbic acid as a protective and Polyethelene glycol as a size controller and capping agent in the synthesis of Copper nanoparticles [40]. Chemical reduction method requires proper reaction condition, pH , temperature and organic and inorganic capping, reducing and stabilizing agent causes non economical and non-ecofriendly process.

2.2 Electrochemical Method

The electrochemical method is more common and easy method of nanoparticle synthesis. In this method Cu and CuO nanoparticles by using Cu as a anode and Cu and other metal as a cathode. During electrochemical treatment particle size of copper nanoparticles can be reduced by increasing the voltage [41]. As the conductivity increases the yield of copper nanoparticles increases [42]. Vikky Anand and coworker synthesized Copper nanoparticle by using this method at different pH value . The copper itself act as a electrode and 0.15 M oxalic acid solution used as a electrolyte . The size of synthesized nanoparticles range of 20 nm to 7 µm. All the particles were mesoporous in nature [43]. Hassan Hashemipour and coworker synthesized the copper nanoparticles by chemical reduction and electrochemical reaction. In the electrochemical deposition method copper nanoparticles were prepared using bath containing homogeneously acidified Copper sulphate solution. the average size of copper nanoparticle is 10 nm. Comparison shows that the quality of copper nanoparticle is better in electrochemical method than in chemical reduction method. pH and fluctuation in voltage affect the size of the copper nanoparticle via electrochemical reduction method [44].

2.3 Microemulsion Method

Synthesis of copper nanoparticle is also done by microemulsion technique because of its ability to control shape and size of nanoparticles by the use of proper microemulsions and surfactant adsorption. Microemulsions are clear, stable, isotropic liquid mixtures of water, oil and surfactant frequently in combination with co-surfactant[45-46]. Hiroyuki Ohde and coworker synthesized the copper and silver nanoparticles in a water in supercritical Carbondioxide microemulsion. Sodium cynobororohydride and NNNN-tetramethyl -p-phenylenediamine are effective reducing agent for synthesizing these metal nanoparticles in the microemulsion [47]. Jignasa Gohel synthesized copper and copper sulphide nanoparticles by microemulsion method. The effect of most crusial oparatiing parameter, water to surfactant molar ratio (w) on the product specification including size distribution and morphology [48].

2.4 Sol Gel Method

The sol–gel process is a wet chemical technique that uses either a chemical solution or colloidal particles to produce an integrated network. Metal alkoxides and metal chlorides are the typical precursors. They undergo hydrolysis or polycondensation to produce colloidal system composed of nanoparticles dispersed in solvent. Then the formation of inorganic continuous network containing a liquid phase took place. Drying process is performed to remove the liquid phase. Then thermal heat treatment is carried out to improve the mechanical properties of prepared nanoparticles [49]. Saja Mahsen Jabbar synthesized Copperoxide nanoparticles via sol gel method using Copper chloride, Sodium hydroxide and Ethanol. The particle size is less than 2µm [50]. Jivan jyoti Mahindru and coworker synthesized the Copper , Silver and Nickel nanoparticles by sol gel method and geraniol act as reducing agent. The synthesized nanoparticles are formed in the size range 50 -100nm [51].

3. Biological Method

The outcomes of the above Chemical report prevailed in the literatures indicate that synthesis of nanoparticles by chemical methods are non-ecofriendly, time consuming, expensive and hazardous to health and environment. There is a growing need to develop environmentally and economically processes, which do not use toxic chemicals in the synthesis protocols. This has conducted researchers to look at the plants and organism. The potential of organisms in nanoparticle synthesis ranges from simple prokaryotic bacterial cells to eukaryotic fungi and plants and animal. The part of plant extract like root, stem and leaf extract is used for green synthesis of copper nanoparticles.

3.1 Bacteria

It is simple, cost effective and reliable method for synthesis of nanomaterial globally in which the microorganism is employed for the synthesis of Copper nanoparticles. The mechanism behind the extracellular synthesis of nanoparticle using microbes is not fully known but it is considered that the enzyme like nitrate reductase secreted by microbe helps in bio reduction of metal ion to metal nanoparticle. Also it requires mild experimental condition like pH, temperature, have easy downstream processing and short generation time for synthesis of nanoparticles [52]. S . shantkriti and coworker synthesized the copper nanoparticles using cell free culture supernatant of nonpathogenic bacteria pseudomonas fluresœns [53]. Hamid Reza Ghorbani and coworker also synthesized copper nanoparticles by using culture supernatants of Salmonella typhimurium. The mean size of copper nanoparticles is 49 nm and the distribution of nanoparticle is narrow 10nm [54].

3.2 Algae

The synthesis of nanoparticle by using algae is the convenient method of nanoparticle synthesis. The molecules present in algae itself act as a reducing, capping and stabilizing agent**.** Anju Arya and coworker synthesized the copper and silver nanoparticles by using green alga Botryococus braunii and its antimicrobial activity. The size of copper nanoparticles is 50 nm with FCC geometry [55]. Priyanka Bhatacharya and coworker synthesized the copper oxide nanoparticles by using green microalgae Anabaena cylindrica. From the FESEM analysis it was observed that rod like nanostructure was formed having dimension of 40-60 nm. The micrographs also showed presence of some larger particles due to the agglomeration with more or less uniform size, shape and morphology [56].

4. Plants: -

Green Synthesis of Silver nanoparticles by using plant parts is most easy, efficient, cost effective and productive method of nanoparticle synthesis. Plants various parts such as leaves, fruits, flowers, bark, stem, seed, roots, latex and some excretory product of plants like gum are used for successful synthesis of copper and other nanoparticles. The change in color of solution after adding extract is the indication of synthesis of nanoparticles. There is no need to add extra reducing, capping or stabilizing agent while preparation as the plant parts already contain the reducing and stabilizing agent like Terpenoid, Caffeine, Phenolic acid including Alkaloids, Proteins, Enzymes, Amino acids, alcoholic compounds, Poly-saccharides, Polyphenols and Flavonoids [57-59]. Synthesis of nanoparticles using plants is cost effective and thus can be used as an economic and valuable alternative for the large-scale production of nanoparticle. Various researcher used the different parts with successful synthesis of nanoparticle.

4.1 Leaf Extract

It is the best and the greenest method of synthesis of copper nanoparticle. In this method freshly prepared leaf extract of plant is added to the metal solution. The leaf extract contain biomolecule itself act as a reducing, stabilizing and reducing agent. Muhammad Asif Asghara and coworker synthesize the copper, iron and silver nanoparticles by using green extract of green and black tea leaves extract. SEM images clearly showed that Fe-NPs, Cu-NPs and Ag-NPs were agglomerated and spherical shaped with a diameter ranging from 42–60-, 26–40- and 10–20 nm, respectively [60]. Hyo-Jeoung Lee synthesize the Copper nanoparticles using Magnolia kobus leaf extract. Electron microscopy analysis of copper nanoparticles indicated that they ranged in average size from 37 to 110nm and could be controlled by changing the reaction temperature and leaf broth concentration. 61 Ill-Min Chung and coworker synthesised the copper nanoparticles using the leaf extract of Eclipta prostrata and study their antioxidant and cytotoxic activities. The synthesized nanoparticles are of 23 to 57 nm with an average size of 31±1.2 nm. The findings of the study suggested that biosynthesized copper nanoparticles that utilize extracts of Euphorbia prostrata may be used for therapeutic application, and thus are a promising nanomaterial [62].

4.2 Flower extrat

The inflorescence and flower extract are also used to synthesize Copper nanoparticle. The biomolecules present in the flower also act as a reducing and capping agent.Volli G and coworker synthesise the copper nanoparticleds using Cassia fistula flower extract. The size of the copper nanoparticles 20nm [63]. Manjiri synthesised the CuO nanoparticles of 20-45 nm by using the flower extract of Aglaia elaeagnoidea and study the catalytic and recyclability properties [64].

Seed Extract also used to synthesize the copper nanoparticles. Akbar Rostami used Rumex cruspus seed extract and study the catalytic application of reduction of dyes. The particle size of CuO nanoparticles on the seashell sheets was in the range of 8–60 nm. Catalytic ability of CuO nanoparticle seashell was investigated for the reduction of 4-nitrophenol (4-NP) and Congo red (CR) [65]. Noshin Nazar synthesize copper nanoparticles by using seed extract of Punica granatum as well as study the photocatalytic activity. The biomolecules in seed extract itself act as a reducing and capping agent. The average size of copper nanoparticles 40-80 nm with semi spherical shaped and uniform distribution [66].

4.3 Latex Extract

Latex is also used in the synthesis of copper nanoparticles. The latex of Calatropis Procera is used. The synthesized copper nanoparticles are of average size 15+ 1.7 nm. FTIR analysis showed that capping behavior of latex protein that contribute to long term stability of copper nanoparticles [67].

4.4 Fruit Extracts

Fruit is also used for the synthesis of copper nanoparticle. Rahollah Khani synthesized the copper nanoparticles .They used the fruit extract of Zizipus spina Cristi . The peel of the fruit is also used for the synthesis of copper nanoparticles [68]. Pavan Kour and coworker synthesise copper nanoparticles using peel extract of Punica granatum. The extract itself act as a reducing and capping agent. The size of the copper nanoparticles is of 15 to 20 nm. The biologically synthesized Copper nanoparticles demonstrated high antibacterial activity against opportunistic pathogens [69] Madiha Batoool synthesise the copper nanoparticles using Solanum Lycopersicum (Tomato Aqueous Extract). The size of the copper nanoparticles is 70-80 nm [70].

5. Antimicrobial activity

Antimicrobial activity of copper nanoparticles is higher than silver nanoparticles. The bactericidal properties of copper nanoparticles are due to the release of copper ion from the particles which confers the antimicrobial activity. The smaller particles have higher antimicrobial activities due the equivalent copper mass contents. Copper nanoparticle get attached to the cell wall there by disturbing the permeability of the cell wall and cellular respiration. The nanoparticles may also penetrate deep inside the cell wall causing cellular damage by interacting with phosphorous and Sulphur contain compound such as DNA and protein present inside the cell wall [71-73].

6. Conclusion: -

This review emphasis the ecofriendly, cost effective and nonhazardous, green method of synthesizing nanoparticles by using plants part extracts which overcomes the other physical and chemical method with all the way. All the other methods require different chemicals, electricity, high temperature, unique microbial culture, light with constant electricity and most important the extra reducing, capping and stabilizing agent. The molecules in plants itself act as a reducing, stabilizing and capping agent. By studying above method we can concluded that the green synthesis of nanoparticle by using plant part extract is more economical, nonhazardous, ecofriendly and effective all the way.

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