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GREEN SYNTHESIS OF DIFFERENT NANOPARTICLES AND THEIR POTENTIAL APPLICATIONS IN DIFFERENT FIELDS- A CRITICAL REVIEW

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ABSTRACT

Nanoparticles (NPs) as its name suggests is a 'nano' or 'dwarf' particle with size ranges from 1nm to 100 nm. NPs synthesis and characterization is done under the field of 'Nanotechnology' which is one of the promising field of science, deals with small dimension material and have potential impact in all field of human life. NPs have broad range of application in electronics, environment and in medical field for drug and gene delivery. Traditionally, different methods have been extensively employed by researchers for NPs fabrication, but chemical as well as physical methods are not suitable due to hazardous chemicals, high cost, and intense labor. Therefore Green Nanotechnology' is used to resolve these drawbacks 'which use plants for NPs synthesis. Green synthesis of NPs reduce the contamination from environment and preserve natural resources, it is cost effective and faster technique that helps in large scale production of NPs. Green Synthesis of NPs from plants depends on the reducing capacity of plants to reduce metal ions. After synthesis of NPs its shape and size characterized by various techniques like UV-VIS spectroscopy, EPMA (Electron Probe Micro Analysis), XRD (X-ray Diffraction), Zeta potential and FTIR (Fourier Transform Infrared) analysis. NPs also have antimicrobial activity which is examined against various microorganisms.

Keywords: **Nanoparticles, Plants, Green synthesis, Drug delivery, Antimicrobial activities.**

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INTRODUCTION

Nanotechnology has evaluated the ultrafine, nano dimension nanoparticles which are of enormous importance because of their exceptionally minute dimension as well as bulky shell area. Scientist from many countries has declared that this is the technology of 21st century. But its development was traced back in 1857, when stable gold colloidal nano size particle was synthesized by Michael Faraday. Also in 1959 Nobel Laureate, 'Richard Feynman' asked the scientist to derive the inspiration from mother nature to make things smaller. However, he did not use the word Nanoscience and Nanotechnology, Moreover; we can see his novel thought by making things small. Nanotechnology term was coined by Professor Norio Taniguchi in 1974[1-4, 67]. NPs roughly clustered in two class, viz. Organic NPs (carbon NPs), Inorganic NPs which have two subclass, one is, Magnetic NPs (novel metal NPs) and second is Semi-conductor NPs (titanium oxide and zinc oxide)[4, 5]. Commercial applications of NPs are increasing day by day due to great interest of nanostructure material in every day's life. Biological method does not meet the industrial demand, Chemical and Physical methods are not environmentally benign, affecting the animal and as well as human health and also not economically safe. Then researchers used Green Nanotechnology, which is novel and innovative approach that leads to develop new novel discoveries in Green Chemistry. Green chemistry implements sustainable process which includes 12 fundamental principles, lead to the synthesis and stabilization of metal NPs[6, 7]. The size and shape of NPs changes according to their method of synthesis and its activity also depends on size, shape and surface chemistry. Plants used for green synthesis of NPs particularly contain extremely burly metal ion hyper accumulating activity as well as reducing capability. NPs can be designed according to the application. Green Nanotechnology has revived metal nanoparticles which received expressing results due to their extraordinary properties and applications. In recent time, synthesis of Gold, Silver, Platinum, Zinc and Copper NPs obtained from plant parts extract[8]. Silver NPs is extensively used novel NPs due to its antibacterial, antiviral and antifungal properties. NPs synthesis from plants involves *invitro* and *invivo* approach. They used solid media with $AuCl4^-$ rich environment. Geranium plant (*Pelargonium graveolens*) leaf broth was used to synthesize Gold NPs[10]. The bioreduction process was rapid and done in aqueous silver nitrate solution, Geranium plant contain protein, terpenoids plus extra bio-organic complexes which participated into bioreduction of silver ions and synthesized NPs that were stable for 4 weeks[10]. It is evidenced that there is *Colletotrichum* sp. fungus associated with Geranium plant can produce taxol and gibberellins compounds with an intergenic genetics exchange between plant and fungus. Vitamin B_2 and Vitamin C used to synthesize gold and platinum NPs also. Biotechnological methods have been used for NPs synthesis[9].

Three main steps in the preparation of NPs through green chemistry are

1)Selection of solvent metal medium, according to type of NPs synthesis.
2) Selection of eco friendly reducing agent, which is plant.
3) Selection of stabilizing agent[6, 13].

There is wide distribution in shape and size of various NPs synthesize from different plants. Protein and peptides participate in altering the NPs shape and affect the yield of NPs. Shape, size and surface morphology play vital role in controlling the overall properties of NPs. High surface energy of the NPs makes them enormously reactive, most of NPs undergoes aggregation without stabilization of their surfaces. First time rod shaped NPs were revealed[9]. Impact of plant biomass on size of NPs increased according to the concentration of biomass [9, 11, 14].

WHY GREEN SYNTHESIS?

Green synthesis is an environmental friendly approach where no toxic chemicals involved[15].

It is a revolutionary technique which leads to new era that unfolds potential of plants in synthesizing stable NPs, increase the life span of NPs synthesized and also overcome the limitations of chemical and physical methods[2, 16]. Plants are known as 'chemical factories', contains various therapeutic compounds, which are used as traditional medicines from ancient era. Various plant biomolecules like phenols and alkaloids are known to evaluate synthesis and stabilization of NPs[2]. Plants rich in genetic variability with number of biomolecules like vitamins, coenzymes based intermediates and excellent reducing agents include phenolic compounds, alkaloids and sterols, metal ions can be reduced into NPs within a single step[17]. Metallic NPs synthesized through plants acts as promising biomedical agents[4]. Whole plant parts like leaves and fruits are used for green synthesis. It is faster and reliable technique comparative to conventional techniques which scale up the process of production of commercially applicable NPs with less or no toxicity. Plants therefore used for NPs synthesis because they actively uptake and reduce metal ions in bioremediation and thereby can form complex metal NPs[18,19.] This technique links the two fields, materials science as well as biotechnology, resulted in Nanobiotechnology. It Works on 12 principles of Green chemistry which include such goals as to prevent waste, increase raw material consumption, explore catalysis and prevent the use of noxious substances, elevated temperature, pressure and power[18-21]. There are various methods of green synthesis which is irradiation method, tollens method, biological method, polysaccharide method and polyoxometallates method[22]. NPs of controlled shape and size are synthesized through plant extract. New drugs are developed from natural products through green synthesis for the reason of resistance of micro-organism toward the conventional medicines[46]. NPs synthesized from medicinal plants are highly toxic for multi-drug resistance microorganisms and various pathogenic bacteria and fungi than conventional antibiotics[46]. The main objective of green nanotechnology is to synthesize NPs of desired properties and required quality[4]. NPs fabricated from plants, have novel applications for benefits of humans than the conventional methods, in degradation of organic pollutants, cytotoxicity, brain cancer, and in bioremediation[4]. One potential benefit of emerald production of NPs is that it is easy and inexpensive to be cultured plant modified materials as compared to microbial one[16].

FACTORS ACCOUNTABLE FOR THE METAL IONS REDUCTION

Various plant products plus metabolites helps during bioreduction of metal ions. Alkanoids, terpenoids, polyphenols, phosphoric acid and polysaccharide affect the bioreduction, for example all these compounds reduce silver and chloroaurate ions in leaf of *Cinnamomum camphora*[1, 8]. Terpenoids are associated with NPs, examined with FTIR and exhibit antioxidant activity. Protein and vitamin C in *Cinnamomum annuum* leaf extract is used for Selenium NPs production[23]. Main terpenoid in *C. zeylanisum* leaf extract detected was Eugenol which has principal activity in reduction of AgNO3 and HAuCl4[8]. Glutathione and Metallothioneins, phytonutrients present in plants that exposed to metal stress and bind xenobiotics respectively and plays novel role in NPs synthesis. Phenolic compounds chelate Reactive Oxygen Species (ROS)[97, 100, 102], Chelation with their carbonyl and hydroxyl group takes place and due to that one of the best participants for NPs synthesis. During glycolysis, H^+ with NAD produced which helps in formation of Nanosilver particle. *S. aucuparia* leaf extract contain sorbate ion which encapsulate NPs and maintain stability[1]. Some scientist investigated that fruit extract of *Emblica officinalis* formed extremely steady gold as well as silver NPs. It is also studied that plant extract contain sugar mainly glucose (monosaccharide) which induce metal NPs synthesis[1, 24]. All 20 amino acids have potential to reduce or bind with metal ions. Tryptophan and Histidine are strongest reducing and binding agents respectively for Au ions. Also the amino acid sequence of protein has influence on size, shape, and amount of NPs[25]. Other than plants internal and external reasons like concentration of metal ions, reaction time, pH, plant biomass and temperature, also

influence the metal NPs synthesis. At high pH small and spherical NPs are formed. There is contrasting statement depends on the plant species for example in *Avena sativa* at pH 3.0 and 4.0 small sized AuNPs are formed. At high temperature, rate and efficiency of NPs synthesis increases, for example in alfalfa plant (*M. sativa*) above 30 °C triangular AgNPs are formed and at above 60 °C in *Cassia fistula* spherical NPs are formed[26, 27].

EXAMPLE OF NANOPARTICLES BIOSYNTHESIS USING VARIOUS PLANTS

Plant origin	Nanoparticles	References
Arbutus unedo	Silver	[28,29]
Moringa oleifera	Silver	[30]
Aloe vera	Gold and Silver	[31]
Cinnamomum camphora	Gold and Palladium	[32]
Nelumbo nucifera	Silver	[33]
Punica granatum	Silver and Gold	[34]
Adhatoda vasica	Silver	[35]
Azadirachta indica	Silver	[36,38]
Brassica nepus	Silver	[36]
Stevia rebaudiana	Silver	[36]
Actaea racemosa	Silver	[39]
Eucalyptus angophoroides	Silver	[39]
Pelargonium graveolens	Silver	[39]
Ceratonia siliqua	Silver	[40]
Averrhoa bilimbi	Gold and Silver	[41]
Coleus aromaticus	Silver	[42]
Cassia tora	Silver	[43]
Ananas comosus	Silver	[44]
Morinda pubescens	Silver	[45]
Boswellia ovalifoliolata	Silver	[46]
Shorea tumbuggaia	Silver	[46]
Svensonia hyderobadensis	Silver	[46]
Avena sativa	Gold	[9]
Cymbopogon flexuosus	Silver and Gold	[47]
Medicago sativa	Gold	[20,8,47]
Emblica officinalis	Silver and Gold	[48]
Rosa berberifolia	Silver and Gold	[49]
Geranium maculatum	Silver and Gold	[49]
Aloe barbadensis	Silver and Gold	[49]
Cucurbita digitata	Silver and Gold	[49]
Ficus carica	Silver and Gold	[50]
Acanthe phylum bracteatum	Silver	[51]

Carica papaya	Silver	[52]
Capsicum annuum	Silver	[53]
Annona reticulate	Silver	[54]
Argemone Mexicana	Silver	[55,56]
Coccinia grandis	Silver	[57]
Rumex hymenosepalus	Silver	[58]
Ocimum tenuiflorum	Silver	[59]
Elaeagnus latifolia	Silver	[60]
Phyllostachys aurea	Silver	[60]
Morus rubra	Silver	[61]
Ficus carica	Silver and Gold	[50]
Camellia sinensis	Gold	[62]
Momordica charantia	Gold	[63]
Allium cepa	Gold	[64]
Lippia citriodora	Gold	[65]
Elettaria cardamomum	Gold	[66]

DIFFERENT TYPES OF NANOPARTICLES

Most of the biomolecules and structures have similar size to NPs thereby NPs find potential application in *invivo* and *invitro* biomedical research. NPs have high desired trait in biocompatibility which includes material performance without showing any systemic and local effects[17]. NPs exhibit strong range of toxicity towards different multi drug resistant human pathogen, which depend upon the size of NPs. NPs have large surface area that attached with the cell membrane of microbes also disturbs function similar to permeability as well as respiration. NPs are new type of cost effective and safe biocidal material. Due to its small size, it act as probes of biological markers, have strong affinity to target particular proteins, high heat and electrical conductivity and delayed particles aggregation based on surface modification and stabilization[69].

SILVER NANOPARTICLES

In nanotechnology, silver NPs have gained the interest of intensive research due to their unique biochemical, chemical, physical property and their application in the area of optics, antimicrobials, catalysis. Silver NPs have more important applications like it is utilized at the same time as discerning covering for lunar energy assimilation and the same as optical receptors intended for biolabeling. Silver NPs have been widely studied and used for centuries because of its inhibitory and antibacterial property, because of its high affinity towards sulfur and phosphorus. Bacterial cell membrane has abundance of sulfur containing proteins with which silver NPs react outside and inside the cell membrane and which affects the viability of bacterial cell leads to increased permeability of bacterial cell membrane. Silver NPs can also react with phosphorus present inside the DNA which results into DNA replication, inactivation and proteins containing sulfur which leads to reticence of enzyme activity which in turn cause the death of bacteria. Upsurge of silver NPs focuses on increasing multiple drug resistance by abuse of antibiotics[17, 69-74, 99].

GOLD NANOPARTICLES

The therapeutic use of gold for revitalization is well known for various diseases like syphilis, epilepsy and tuberculosis. Gold NPs is specifically and widely used against microorganism because of their compatibility. They are organically static however been able to be processed to have chemical and photothermal nature. Gold NPs absorbs near infrared irradiation and can kill bacterial and cancer cells via thermal heating. It has been

used as chemotherapeutic agent for various drug resistant microorganisms for example efficacy of vancomycin antibiotic enhanced when covering through gold NPs in opposition to Vancomycin-resistant enterococci (VRE). Reduced gold NP with Cofactor have antimicrobial action in opposition toward gram +ve and gram -ve bacteria the same as Cofactor prevent the formation of peptidoglycan layer after that cell wall become porous then further gold NPs make holes in cell wall which tend to the outflow of contents of cell as well as death of cell[17, 75-80].

PLATINUM NANOPARTICLES

Platinum NPs firstly reported with size ranges from 2-12 nm, was synthesized with *Diopyros kaki* leaf extract. Platinum NPs are useful in water electrolysis[81, 82].

ZINC NANOPARTICLES

Spherical shaped Zinc NPs was synthesized for the first time with *Calotropis procera* as reducing agent. Zinc NPs have evolved as potent antimicrobial agent and are semiconductor material because it is used in ceramics, solar cells, catalysts, and gas sensors[67]. It has been found highly toxic and stable among various metal NPs. It is selectively toxic for bacteria in addition to show negligible consequence on human being cells thus used in food industry and agriculture. Various mechanisms proposed to describe the antibacterial property of zinc NPs like as increase the membrane permeability, disintegrate the cell membrane, and generate hydrogen peroxide and Zn^{2+} ions that damage cell membrane which result in inhibition of the bacterial growth[83].

ALUMINIUM NANOPARTICLES

Aluminium NPs have growth inhibitory effect at high concentration due to surface charge interactions between cells and NPs. Aluminium is stable at high temperature, aluminium NPs contains a positive charge at neutral pH on its surface that interacts with the negatively charged *E. coli* along with polymer bridging and hydrophobic interactions. Antimicrobial property of aluminium NPs is because of the production of ROS that grounds commotion of cell wall in addition to result in death of cell[84-86].

PROPERTIES OF NANOPARTICLES

NPs have fascinating and unusual properties with vast applications more than their bulk equivalents[67]. NPs enable the reaction faster and act as efficient catalyst[16]. NPs have distinct properties due to its varying chemical composition, controlled polydispersity, various sizes and shapes[36]. NPs are advantageous because it is highly fluorescent, biocompatible, good photostable, nontoxic and soluble[61]. There are some key advantages of NPs in drug delivery that they enhance aqueous solubility, increase resistance time, and clearly target the drug to specific location in the body[68]. Metal nanoparticles exhibit antiviral property due to the interior matter as well as shell of ligands. Silver NPs bring to bear defiant viral property in opposition to HIV-1 by early stage of virus replication, inhibit viral entry and act as virucidal cause for together cell associated virus as well as cell free virus because it avoid CD4-dependent virion fastening, infectivity along with fusion[87]. Gold NPs also carries anti-HIV activity when coated with amphiphilic sulphate ended ligand that binds with glycoprotein gp120 present on HIV envelope, prevent the HIV infection. Affinity of NPs increase for gp120 when density of ligand increases[88]. Silver NPs contains high antifungal property against *Candida spp.* Silver NPs target the yeast cell membranes by the formation of pores which result in disruption of membrane potential and in turn cell death[89]. NPs have antibacterial properties against different bacteria[101, 103].

POTENTIAL APPLICATIONS OF NANOPARTICLES

Nanoparticles comprise potential antimicrobial agents against various pathogenic microorganisms therefore applied the same as additives in industrial, consumer and fitness associated goods like as catheters, bandages along with additional material use toward heal wound and burns to prevent infection. NPs are currently used in many household products like washers, shampoo, deodorants, paints, water purification system, bedding and kitchen

utensils. Titanium NPs are permitted by American FDA intended regarding the application into drugs and mankind victuals. Zinc NPs are used for dermatological application in lotions, ointments and creams for its antimicrobial properties[90,91].

NANOPARTICLES IN BIOSENSOR

Metal NPs are feasible in different biological and electrochemical sensing system due to its chemical and physical property. NPs are coated with biological or molecular materials such as antibodies and collagen which act as bioinorganic interface. By controlling NPs size efficient fluorescent probe can be created that release fine illumination in broad array of wavelength. DNA and protein can be immobilized on surface of NPs after that intensity and wavelength of NPs are observed and acts as a DNA and protein biosensor respectively[92, 93].

NANOPARTICLES IN BIOLOGY AND MEDICINE

NPs have greatest value in developing medical diagnostics and treatments. NPs act as fluorescent imaging agent which delivers to cell and then explain the entry of biological material like peptides inside the cell. Silver NPs are mainly used because it provides better absorption of light thus shows stronger and sharper Plasmon resonance[93, 94, 98].

NANOPARTICLES IN DRUG AND GENE DELIVERY

NPs include nanospheres and nanocapsules into which medicine is liquefied, absorbed and detached into the surrounding substance plus drug is bounded to an aqueous covered by a shell like wall respectively. NPs can overcome the drawback like short circulation leads to frequent administration and undesired targeting related to the small therapeutic agents. Polymer NPs can extend the invivo circulation time from minutes to hours (highly stable); with leaky blood vessels this increases the passive delivery of drug to tissue (control drug release from matrix) and feasibility of administration through various routes that is inhalation and oral administrations. Gene delivery via NPs can replace defective or missing gene, delivered gene can cause the destruction of defective cell and cause defective cells to revert back to normal cell[93-96].

NANOPARTICLES IN CANCER TREATMENT

A conventional therapy for cancer which includes radiation, chemotherapy, surgery and hormone therapy have some limitations as they nonspecifically affects the human body both normal and cancerous cell. NPs can overcome the limitations of conventional therapy as it is used as drug delivery agent which loads the drug in greater amount to the tumor site thus improves cancer treatment. NPs act as tumor specific biomarker and imaging capability which diagnose cancer. In the mid 1980s first clinical trial of NPs for anti-cancer drug delivery was done and in 1995 first NPs had entered in pharmaceutical market. NPs are designed as pH and temperature sensitive so can release drug within more acidic environment thus acts as potential tool for cancer treatment[44, 93, 98].

CONCLUSION

NPs are versatile and magical tool for various application its conventional preparation methods physical, chemical and biological are somewhat, somewhere not feasible for safety and stability purpose thus green synthesis method for NPs production have developed which overcome the limitations related with traditional methods. Plant synthesized metal NPs are more stable, safe and easily scaled up. For the future developmental point of view genetically modified plants can improve the properties of nanoparicles.

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