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Review: Green Synthesis of Silver and Gold nanoparticles

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Nanotechnology is a field that is mushrooming, making an impact in all spheres of human life. Nanobiotechnology represents an economic alternative for chemical and physical methods of nanoparticles formation. Presently available literature revealed that the NP synthesis using marine plants, microrganisms and algae as source has been unexplored and underexploited. The development of green processes for the synthesis of NP is evolving into an important branch of nanotechnology. It has many advantages such as, ease with which the process can be scaled up, economic viability, etc. Presently, the researchers are looking into the development of cost-effective procedures for producing reproducible, stable and biocompatible AgNPs and AuNPs. Antibiotic resistance is the world's major public healthcare problem. AgNPs and AuNPs particles play a vital role in nanobiotechnology as biomedicine against Drug-resistant bacteria.

Keyword: Nanotechnology, Nanoparticles, Biomedicine, Drug-resistant bacteria.

1. Introduction

The word "nano" is used to indicate one billionth of a meter or 10^{-9}. Nanoparticles are clusters of atoms and their size from 1–100 nm. "Nano" is a Greek word meaning extremely small. Nanotechnology is a field that is vast in making an impact in all fields of human life. Nanobiotechnology represents an economic alternative for chemical and physical methods of nanoparticles formation. Nanoparticles (NP) attract greater attention due to their various applications in different fields including "nanomedicine". The term Nanotechnology was coined by Professor Norio Taniguchi of Tokyo ScienceUniversity in the year 1974. Nanoparticles can be broadly grouped into two, namely, organic nanopartilces which includecarbon nanoparticles (fullerness) while, some ofthe inorganic nanoparticles include magneticnanoparticles, noble metal nanoparticles (like gold and silver) and semi-conductor nanoparticles (like titanium oxide and zinc oxide). Now a day's scientists are expanding interest in inorganic nanoparticles i.e of noble metal nanoparticles (Gold and silver) as they provide superior material properties with functional versatility.Metallic nanoparticles are most promising and remarkable biomedical agents. Silver, Aluminum, Gold, Zinc, Carbon, Titanium, Palladium, Iron, Fullerenes and Copper have been routinely used for the synthesis of nanoparticles. The use of AuNPs dates back to the 16th century, used for medical, staining and other purposes. There is a growing need to develop environmentally friendly processes through green synthesis and other biological approaches.

2. Importance of the study

Presently available literature revealed that the NP synthesis using marine plant, microrganisms and algae as source has been unexplored and underexploited. Resistance to antimicrobial agents by pathogenic bacteria has emerged in recent years and is a major health problem. Seaweeds or benthic marine algae are the group of plants that live either in marine or brackish water environment. The use of marine algae in the synthesis of AuNPs emerges as an ecofriendly and exciting approach. Utilizing a biological source gives an easy approach, easy multiplication, and easy increase of biomass and size uniformity Antibiotic resistance is the world's major public healthcare problem. Combating the Drug-resistant bacteria is another important challenge. People who become infected with drug-resistant microorganisms usually spend more time in the hospital and require a form of treatment that uses two or three different antibiotics and is less effective, more toxic, and more expensive [1]. The development of green processes for the synthesis of NP is evolving into an important branch of nanotechnology [2-3]. Plants have evolved in the presence of natural Nanomaterials. However, the probability of plant exposure to Nanomaterials has increased to a greater extent with the ongoing increasing production and use of engineered nano materials in a variety of instruments and goods. Plant mediated synthesis of metal nanoparticles is gaining more importance owing to its simplicity, rapid rate of synthesis of NP of attractive and diverse morphologies and elimination of elaborate maintenance of cell cultures and eco-friendliness. The reason for selecting plant for Biosynthesis is because they contain reducing agents like Citric acid, Ascorbic acids, flavonoids, reductases and dehydrogenases and extracellular electron shuttlers that may play an important role in biosynthesis of metal nano particles [4].

2.1 Significance of AgNPs

It has been positioned as the 47th element in the periodic table, having an atomic weight of 107.8 and two natural isotopes 106.90 Ag and 108.90 Ag with abundance of 52 and 48% where as the colloidal silver is of particular interest because of distinctive properties such as good conductivity, chemical stability, catalytic and antibacterial activity [5]. The medicinal and preservative properties of silver have been known for over 2,000 years. It is a rare, but naturally available, slightly harder than gold and very ductile and malleable. AgNPs of many different shapes (spherical, rod-shaped, truncated, triangular nanoplates) were developed by various synthetic methods. Truncated triangular silver nanoplates were found to show the strongest anti-bacterial activity. The AgNPs have excellent antimicrobial property compared to other salts due to their extremely large surface area, which gives good contact with microorganisms. Silver ions and nanoparticles are highly toxic and hazardous to microorganisms. AgNPs have many applications like they might be used as spectrally selective coatings for solar energy absorption and intercalation material for electrical batteries, as optical receptors, as catalysts in chemical reactions in biolabelling, and as antimicrobials. [6-7, 8]. Synthesis of AgNPs using plant [9-13], fungal [14], Bacteria extracts [15]. Antimicrobial and cytotoxic effects of AgNPs. Current research in inorganic nanomaterials having good antimicrobial properties has opened a new era in pharmaceutical industries. Silver is the metal of choice as they hold the promise to kill microbes effectively. AgNPs have been recently known to be a promising antimicrobial agent that acts on a broad range of target sites both extracellularly as well as intra-celluarly.The resistance conferred by bacteria to silver is determined by the 'sil' gene in plasmids [16]. AgNPs have exhibited antimicrobial effect on *Staphylococcus aureus* and *E. coli* [17]. NP take advantages of the oligodynamic effect that silver has on microbes [18]. Green Synthesis of Small AgNPs Using Geraniol and Its Cytotoxicity against cancer cell line Fibrosarcoma-Wehi 164 [19]. Whereas the cell proliferation was evaluated by a modified Crystal Violet colorimetric assay [20]. Green synthesis, antimicrobial and cytotoxic effects of AgNPs using *Eucalyptus chapmaniana* leaves extract [21]. Antimicrobial activities of AgNPs

already done *Azadirachta indica* (Neem) leaves [22]. Several scientists reported green synthesis of AgNPs using plant extracts such as *Acalypha indica* leaf [23], *Jatropha curcas* seeds [24], *Banana* peel [25], *Chenopodium album* leaf [26], *Rosarugosa* [27], *Trianthema decandra* roots [28], *Ocimum sanctum* stems and roots [29], *Sesuvium portulacastrum* leaves [30], *Murraya koenigii* (curry) leaf [31], *Macrotyloma uniflorum* seeds [32], *Ocimum sanctum* (Tulsi) leaf [33], *Garcinia mangostana* (mangosteen) leaf [34], *Stevia rebaudiana* leaves [35], *Nicotiana tobaccum* leaf [36], *Ocimum tenuiflorum, Solanum trilobatum, Syzygium cumini, Centella asiatica,* and *Citrus sinensisleaves* [37], *Arbutus unedo* leaf [38], *Ficus benghalensis l*eaf [39], *Mulberry* leaves [40], and *Olea europaea* leaves [41]. Currently AgNPs are wildly used as antibacterial and antifungal agents in a diverse range of consumer products: air sanitizer sprays, detergents, soaps, shampoos, and washing machine [42]. In the Synthesis of AgNPs carob leaf extract shown better speed in compared with other extracts [43]. The synthesis of stable AgNPs by the bioreduction method was investigated. Aqueous extracts of the manna of hedysarum plant and the soap-root (*Acanthe phylum bracteatum*) plant were used as reducing and stabilizing agents [44]. Preparation of nanoscaled gold materials has become very important due to their unique properties, which are different from those of the bulk materials [45].

2.2 Significance of AuNPs Particles

Gold is a well known biocompatible metal and colloidal gold was used as a drinkable solution that exerted curative properties for several diseases in ancient times [46]. AuNPs have a great bactericidal effect on a several range of microorganisms; its bactericidal effect depends on the size and shape of the particle [47] Recently there are a few, reports that algae is being used as a important biosource for synthesis of metallic nanoparticles [48]. AuNPs have wide range of applications in nano-scale devices and technologies due to its chemical inertness and resistance to surface oxidation [49]. AuNPs play a vital role in nanobiotechnology as biomedicine because of convenient surface bioconjugation with biomolecular probes and remarkable plasmon-resonant optical properties [50-52]. Many research articles reported the synthesis of AuNPs using plant extracts such as *Ficus religiosa* [53], *Memecylon umbellatum* [54], *Macrotyloma uniflorum* [55], *Brevibacterium casei* [56,57], *Citrus limon*, *Citrus reticulata* and *Citrus sinensis* [58], *Piper pedicellatum* [59], *Terminalia chebula* [60], *Memecylon edule* [61], *Nyctanthes arbortristis* [62], *Murraya Koenigii* [63], *Mangifera indica* [64], *Banana peel* [65], *Cinnamomum zeylanicum* [66], *Cochlospermum gossypium* [67], *Euphorbia hirta* [68]. AuNPs have an important function in the delivery of nucleic acids, proteins, gene therapy and *in vivo* delivery, targeting, etc [69]. In the recent decade, gold nanoparticles (NPs) [70] have attracted significant interest as a novel platform for various applications such as nanobiotechnology and biomedicine. Nano size gold, an emerging nanomedicine is renowed for its promising therapeutic possibility high surface reactivity, resistance to oxidation and plasmon resonance [71]. Biogenic gold nanotriangles and spherical AgNPs were synthesized by a simple procedure using *Aloe vera* leaf extract as the reducing agent. The kinetics of gold nanotriangle formation was followed by UV-vis-NIR absorption spectroscopy and transmission electron microscopy (TEM) [72]. GGFE can provide an environmentally benign rapidroute for synthesis of AuNPs that can be applied for various purposes. Biogenic AuNPs synthesized using GGFEexhibited excellent chemocatalytic potential [73].

3. Activities of AuNPs

The results showed that the leaf extract of menthol is very good bioreductant for the synthesis of AgNPs and AuNPs and synthesized NP active against clinically isolated human pathogens, *Staphylococcus aureus* and *E. coli*. [74]. The antibacterial efficacy of AuNPs increases because of their larger total surface area per unit [75]. AuNPs have antibacterial [76, 77]. The ability of AgNPs to release silver ions is a key to their bactericidal activity [78]. Ionic forms of gold shown to have cytotoxicity on various cell types and adverse effects on red blood cells [79]. The

study was conducted to prepare ~20 nm AuNPs by a chemical reduction method and evaluate their cytotoxicity by MTT assay using human dermal fibroblasts–fetal (HDF-f) [80], The toxicity of starch-coated AgNPs was studied using normal human lung fibroblast cells (IMR-90) and human glioblastoma cells (U251). The toxicity was evaluated using changes in cell morphology, cell viability, metabolic activity, and oxidative stress [81]. AuNPs important activities like anticoagulant activity [82], anticancer [83-85].

4. Factors affecting biosynthesis of nanoparticles

Both AgNPs and AuNPs can be successfully synthesized by traditionally chemical and physical methods. However, these methods strongly depend on severe reaction conditions, for example, aggressive agents like sodium borohydride, hydrazinium hydroxide, cetyltriethylammnonium bromide, and harmful solvent system to environment and ecology, higher temperature and higher pressure have been used. Temperature plays an important role to control the aspect ratio and relative amounts of gold nanotriangles and spherical nanoparticles. Temperature variations in reaction conditions results in fine tuning of the shape, size and optical properties of the anisotropic nanoparticles [86]. The catalytic activity of nanoparticles dependent on various parameters like their size as well as their shape, size distribution, structure, and chemical–physical environment. The size of AuNPs was shown to increase at higher reaction temperatures as explained by an increase in fusion efficiency of micelles which dissipates supersaturation [87]. pH of the medium influence the size of nanoparticles at great concern. Other than pH and temperature other factors also play role in NP synthesis. The sizes of AuNPs decreases with increasing NaCl concentrations (size ranges, 5-16 nm) synthesized without addition of NaCl (size ranges 11-32 nm) [88].

5. Synthesis and characterization of AuNPs

(a) an aqueous chloroauric acid solution (10-3 M)was added separately to the reaction vessels containing the ethanol extract of black tea and its tannin free fraction (10% v/v), and the resulting mixture was allowed to stand for 15 min at room temperature. Chloroa uric acid was purchase from Merck, Darmstadt, Germany. The ethanol solution (10% v/v) was used as a negative control. The reduction of the Au+3 ions by these ethanol extracts in the solutions was monitored by sampling the aqueous component (2 ml) and measuring the UV–visible spectrum of the solutions. All samples were diluted three times with distilled water and the UV–visible spectra of these samples were measured on a Labomed Model UVD-2950 UV-VIS Double Beam PC Scanning spectrophotometer, operated at are solution of 2 nm. Furthermore, AuNPs were characterized by transmission electron microscopy (model EM 208 Philips) [89].

(b) In the synthesis of AuNPs, 10 ml of the aqueous extract of *Gracilaria corticata* was added to 90 ml of 10-3 M aqueous HAuCl4 solution in 500ml Erlenmeyer flask and stirred for 4 hr at 120 rpm at 40o C. Suitable controls were maintained throughout the conduct of experiments [90].

6. Synthesis of AgNPs

In a typical reaction procedure, 5 ml of plant extract was added to 100 ml of 1 × 10−3 M aqueous AgNO3solution, with stirring magnetically at room temperature. The yellow color of the mixture of silver nitrate and plant extract at 0 min of reaction time changed very fast at room temperature after 2 min to a black suspended mixture. The concentrations ofAgNO3 solution and leaf extract were also varied at 1 to4 mM and 5% to 10% by volume, respectively. UV visible (UV–vis) spectra showed strong surface Plasmon resonance (SPR) band at 420 nm and thus indicating the formation of AgNPs. The AgNPs obtained by plant extract were centrifuged at 15,000 rpm for 5min and subsequently dispersed in sterile distilled water to get rid of any uncoordinated biological materials [91]. Polyphenols found in various plant extracts used as reductants and as capping agents during synthesis. NPs in a single-step green synthesis process and biogenic reduction of metal ion to

base metal is quite rapid, readily conducted at room temperature and pressure, and easily scaled up [92, 93].

7. Characterization of AgNPs and AuNPs

Characterization of nanoparticles is important task to understand and control over nanoparticles synthesis and applications and can be done using techniques such as transmission and scanning electron microscopy (TEM, SEM), atomic force microscopy (AFM), dynamic light scattering (DLS), X-ray photoelectron spectroscopy (XPS), powder X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), and UV–Vis spectroscopy [94].

8. Applications

The use of nanoparticles for biomedical applications, such as drug and gene delivery, biosensors, cancer treatment, has been extensively studied throughout the past decade [95-105]. Toxicity of silver nanoparticles is not fully understood even it is using from long time. Very recently, nanoparticles have gained significance in the field of Biomedicine. Plants and plant extracts can be effectively used in the synthesis of gold and AgNPs as a greener route. Shape and size control of nanoparticles is easily understood with the use of plants. The nanoparticles extracted from plants are used in many applications for benefit of humans. AgNP can also be used for treatment of like cancer [106]. Cytotoxic effects of silver on bacteria have been shown for a wide range of bacterial species. The use of AgNPs and AuNPs in drug delivery systems might be the future thrust in the field of medicine. AgNPs are used in the treatment of epilepsy, venereal infections, acnes and leg ulcers. The Green chemistry synthetic route can be employed for both silver and gold silver nanoparticles synthesis. Among the AgNPs, the biological organisms such as bacteria, fungi and yeast or several plant biomassor plant extracts have been used for nanoparticles synthesis used for a number of applications from electronics and catalysis to biology.

9. Conclusion

The "green" route for nanoparticle (NP) synthesis is of great interest due to eco-friendliness, economic prospects, and feasibility and wide range of applications in nanomedicine, new category catalysis medicine, nano-optoelectronics, etc. It is a new and emerging area of research in the scientific world, where day-by-day developments is noted in warranting a bright future for this field. This green chemistry approach toward the synthesis of AgNPs and AuNPs have many advantages such as, ease with which the process can be scaled up, economic viability, etc. It was concluded that plant mediated synthesis of AgNPs possess potential antimicrobial, anticoagulant activity, anticancer activities. The characterization analysis proved that the particle so produced in nano dimensions would be equally effective as that of antibiotics and other drugs in pharmaceutical applications. The on-going research efforts are focussed on evaluating the safety of nanomedicine and formulating the international regulatory guidelines for the same, which is critical for technology advancement. With vast technology push, there are many challenges head that need to be understood and solve in order to make the NP-based products commercially-viable. Presently, the researchers are looking into the development of cost-effective procedures for producing reproducible, stable and biocompatible AgNPs and AuNPs from bioresources.

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