A Review on the green synthesis, and application of silver nanoparticles

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***Abstract* - Nanoparticles deals with particles having size in the range 1nm-100nm. Nanoparticles of noble metals such as silver show distinct physical, chemical and biological properties which vary according to their varying sizes and are also significantly different from the bulk silver materials. Their unique properties are due to their extremely small particle dimension, high surface area, size quantization effect and several other factors. Silver nanoparticles exhibit electromagnetic, optical, catalytic properties and these properties are highly influenced by the shape and size distribution of the nanoparticles. Silver nanoparticles of different size and shapes can be synthesized by tuning the various synthetic routes. Silver nanoparticles are recognized for its widespread applications also. So this review deals with the green synthetic procedures and applications of silver nanoparticles in medicine.**

***Keywords*- Silver nanoparticles, Green reduction method, Antibacterial activity.**

1. INTRODUCTION

Nanotechnology is an emerging field of science which involves the synthesis and development of various nanomaterials **[1].** It can be defined as a whole knowledge on fundamental properties of nano-sized objects**[2-4]**.The term 'nano' indicates one billionth or 10^{-9} units. It is universally accepted that nanoparticles are clusters of atoms in the size range of 1-100nm.**[5]**

Nanoscience has been established recently as a new interdisciplinary science.**[6]** At present time nanochemistry becomes one of the main growing directions of nanoscience**[4].** Advances in this field largely depend on the ability to synthesize nanoparticles of various nano materials, based on their sizes, and shapes, as well as their efficiency to assemble them into complex architectures [**7**]. Nanotechnology provides the ability to engineer the properties of materials by controlling their size, and this has driven research towards a multitude of potential uses for Nanomaterial [**8**].

With the evolution of nanomedicine as a study for treating infections, metallic silver in the form of nanoparticles has regained its significance [**9,10**]. Several bacteria have developed resistance against antibiotics, which has challenged the treatment of human infections[**11-13**]. Therefore, silver nanoparticles (AgNPs)as an antimicrobial agent seems to be beneficial compared to antibiotics[**14**].

Silver nanoparticles have been the prime focus of the nanoparticles' research industry due to their unique thermal [**15**], electrical [**16**] and optical [**17**] properties and also because of the use of these structures in products that range from photovoltaics [**18**] to biological and chemical sensors [**19**]. In recent years nanoparticles of silver have been found to exhibit interesting antibacterial activities [**20,21**].Antibacterial activity of the silver-containing materials can be used, for example, in medicine to reduce infections as well as to prevent bacteria colonization on prostheses[**22**], catheters[**23,24**],vascular grafts[**25**], dental materials[**26**], stainless steel materials[**27**] and human skin[**26,28**]. Contrary to bactericide effects of ionic silver, the antimicrobial activity of colloid silver particles are influenced by the dimensions of the particles, the smaller the particles, the greater the antimicrobial effect [**20**].The catalytic activity of the silver nanoparticles id greatly ruled by their size, structure,shape,size distribution and chemical- physical environment. Thus proper control of the shape and size distribution of these nanoparticles is necessary. The specific control of shape, size , and size distribuition is achieved by varying the synthetic strategies, reducing agents and stabilizers**[6].**

Biosynthesis of silver nanoparticles using plant extracts may be influenced directly or indirectly by photochemical in extracts such as phenols, flavonoids and antioxidants as well as the physicochemical factors governing the kinetics of the reactions.This route is preferably docile as it is ecofriendly, involves less energy intensive processes and is cost effective. Moreover, it is an efficient way of waste biomass utilization for the biosynthesis of silver nanoparticles. Currently silver nanoparticles are prepared by different methods including electrolysis, physical, chemical and biological methods [**29, 30**]. The bio reduction of silver ions to yield silver nanoparticles seems to be an efficient, cost effective and eco friendly approach. Biosynthesis of silver nanoparticles using the plant extracts of *Lippia citriodora* [**31**], *Citrus sinensis* [**32**], *Magnolia kobus* [**33**], neem leaf, geranium leaf [**34**] have already been reported.

2. GREEN SYNTHESIS OF SILVER NANOPARTICLES

2.1 Green synthesis of silver nanoparticles using plant parts

The use of plant parts for the synthesis of silver nanoparticles has drawn attention because of its rapid, eco-friendly,cost-effective, easy approach for biosynthetic processes. The reduction and stabilization of silver ions by combination of biomolecules such as proteins, aminoacids, enzymes, polysaccharides, alkaloids, tannins, phenolics, saponins, terpenoids and vitamins which are already established in the plant extracts having medicinal values and are environmental benign, yet chemically complex structures**[35].**

In this procedure the various parts of the plant such as fresh leaves, stem, fruit, fruit peel,seed etc are finely cleansed and boiled in 100mL distilled water contained in conical flask. This plant extract was then added to 1mM silver nitrate solution and heated at about 80^{o}C for few hours. Change in colour of the solution to reddish brown will be observed during the heating process after 15-20 mins. The resulting solution then needs to be centrifuged at 10,000 rpm for about 25mins.The centrifuged sample was then collected and vacuum dried for analysis**[36-39].** These plant extracts contain biomolecules, which act as both reducing and capping agents that form stable and shape-controlled nanoparticles. Main compounds which affect the reduction and the capping of the nanoparticles are biomolecules such as phenolics, terpenoids, polysaccharides, flavones, alkaloids, proteins, enzymes, amino acids, and alcoholic compounds. However, quinol and chlorophyll pigments, linalool, methyl chavicol, eugenol, caffeine, theophylline, ascorbic acid, and other vitamins have also been reported. The nontoxic phytochemicals including aforementioned flavonoids and phenols have unique chemical power to reduce and also effectively wrap nanoparticles, thus preventing their agglomeration. Phenolic compounds possess hydroxyl and carboxyl groups, which are able to bind to metals.**[40]**

Table 1. Green synthesis of silver nanoparticles by different researchers using plant extracts.[41]

Plants	Size (nm)	Plant's part	Shape
Alternanthera dentate	50–100	Leaves	Spherical
Acorus calamus	31.83	Rhizome	Spherical
Boerhaavia diffusa	25	Whole plant	Spherical
Tea extract	20–90	Leaves	Spherical
Tribulus terrestris	16–28	Fruit	Spherical
Cocous nucifera	22	Inflorescence	Spherical
Abutilon indicum	7–17	Leaves	Spherical
Pistacia atlantica	10–50	Seeds	Spherical
Ziziphora tenuior	8–40	Leaves	Spherical
Ficus carica	13	Leaves	–
Cymbopogan citratus	32	Leaves	–
Acalypha indica	0.5	Leaves	–
Premna herbacea	10–30	Leaves	Spherical
Calotropis procera	19–45	Plant	Spherical
Centella asiatica	30–50	Leaves	Spherical
Argyreia nervosa	20–50	Seeds	–
Psoralea corylifolia	100–110	Seeds	–
Brassica rapa	16.4	Leaves	–
Coccinia indica	10–20	Leaves	–
Vitex negundo	5 & 10–30	Leaves	Spherical & fcc
Melia dubia	35	Leaves	Spherical
Portulaca oleracea	<60	Leaves	–
Thevetia peruviana	10–30	Latex	Spherical
Pogostemon benghalensis	>80	Leaves	–
Trachyspermum ammi	87, 99.8	Seeds	
Swietenia mahogani	50	Leaves	
Musa paradisiacal	20	Peel	
Moringa oleifera	57	Leaves	
Garcinia mangostana	35	Leaves	
Eclipta prostrate	35–60	Leaves	Triangles, pentagons, hexagons
Nelumbo nucifera	25–80	Leaves	Spherical, triangular

Plants	Size (nm)	Plant's part	Shape
Acalypha indica	20–30	Leaves	Spherical
Allium sativum	4–22	Leaves	Spherical
Aloe vera	50–350	Leaves	Spherical, triangular
Citrus sinensis	10–35	Peel	Spherical
Eucalyptus hybrid	50–150	Peel	
Memecylon edule	20–50	Leaves	Triangular, circular, hexagonal
Nelumbo nucifera	25–80	Leaves	Spherical, triangular
Datura metel	16–40	Leaves	Quasilinear superstructures
Carica papaya	25–50	Leaves	
Vitis vinifera	30–40	Fruit	

2.2 Green synthesis of silver nanoparticles using bacteria

Synthesis of Silver nanoparticles by microbes is due to their defense mechanism (resistance mechanism), and this is how the nanoparticles produced are useful to us. The resistance caused by the bacterial cell for silver ions in the environment is responsible for its nanoparticles synthesis. The silver ions in nature are highly toxic for the bacterial cells. So their cellular machinery helps in the conversion of reactive silver ions into stable silver atoms. The nanoparticles can be artificially synthesized in vitro using chemical method via ethanol. But, here the synthesis was done through E. coli under room temperature. The supernatant was taken from the nutrient broth, incubated overnight inoculated with E. coli. Then 1 mM of AgNO3 (1% v/v) was added to the supernatant. The formation of silver nanoparticles was observed within 10 minutes. The color change was noticed from fine yellow color to reddish brown with time.**[42]**

2.3 Green synthesis of silver nanoparticles using fungi

Similar to bacteria, due to their tolerance and metal bioaccumulation ability, high binding capacity, and intracellular uptake, fungi have been of interest in biological production of the metallic nanoparticles. Compared to bacteria, fungi are simpler to handle in a laboratory process. The mechanism of nanoparticle production using fungi is different; fungi secrete large amounts of enzymes which are used to reduce silver ions that induce the formation of the metal nanoparticles **[40].**

3. BIOMEDICAL APPLICATIONS OF SILVER NANOPARTICLES

3.1 Antibacterial effects

Silver nanoparticles have antibacterial properties and can inhibit the reproduction of bacteria, which is a microbe. The silver nanoparticles can "inactivate proteins, blocking respiration and electron transfer, and subsequently inactivating the bacteria" **[43].** Inactivation of the bacteria does not allow them to reproduce. The nanoparticles are able to interact with the microbes because the "cell wall peptidoglycans contain negatively charged molecules that will likely interact electrostatically with the silver ions" **[44].** The silver nanoparticles naturally have a positive charge, which causes them to be attracted to the negatively charged molecules within the cell wall and causes damage to the cell by interrupting its natural processes. The antibacterial properties of the silver nanoparticles depend on the size of the particles; the smaller the size the greater the effect. The particle size is a major factor because the smaller the particle the greater the surface area, which allows for greater interaction with the bacteria. "Nanoparticles and silver ions interact with sulfur-containing compounds found in bacterial membrane protein and with phosphorous-containing compounds, such as DNA" **[43].**The interaction with the DNA can also cause a decrease in microbe reproduction, allowing the antimicrobial effects on surfaces to be successful.**[45]**

3.2 Antiviral effects

Metal nanoparticles have been studied for their antimicrobial potential and have proven to be antibacterial agents against both Gram-negative and Gram-positive bacteria. Theoretically, any metal could be analysed for antiviral activity, however, little effort has been done to determine the interactions of metal nanoparticles with viruses, and only recently some studies have emerged showing that metal nanoparticles can be effective antiviral agents against HIV-1, hepatitis B virus, respiratory syncytial virus, herpes simplex virus type 1 monkeypox virus, influenza virus and Tacaribe virus**[46]**

The antiviral effects of Ag-NPs, most publications have suggested that Ag-NPs could bind to outer proteins of viral particles, resulting in inhibition of binding and the replication of viral particles in cultured cells. Although the antiviral mechanism of Ag-NPs has not been fully known yet, Ag-NPs are still suggested as potential antiviral agents in the future [47].

3.3 Anti-fungal effects

Kim *et al* studied the antifungal activities of Ag-NPs against a total of 44 strains of six fungal species from clinical isolates and ATCC strains of *Trichophyton mentagrophytes (T. mentagrophytes)* and *Candida albanicans* (*C. albanicans*). Results showed 80% inhibitory concentration (IC80) from 1 to 7 μg ml−1. The antifungal activity of Ag-NPs against *C. albanicans* could be exerted by disrupting the structure of the cell membrane and inhibiting the normal budding process due to the destruction of the membrane integrity.Roe *et al* have tested the antifungal activity of plastic catheters coated with Ag-NPs (~100 nm thick), and results showed that the growth inhibition was almost complete for *C. albicans*. Pamacek *et al* investigated the antifungal activity of Ag-NPs prepared by the modified Tollens process. Results also revealed the minimum inhibition against *C. albicans* growth at 0.21 mg −1 using naked Ag-NPs, and 0.05 mg l−1using Ag-NPs modified with sodium dodecyl sulfate (SDS). Additionally, Ag-NPs effectively inhibited the growth of the tested yeasts at the concentrations below their cytotoxic limit against the tested human fibroblasts determined at a concentration equal to 30 mg l−1 of Ag-NPs. Other publications also reported MICs of Ag-NPs from 0.4 to 3.3 μg ml−1 against *C. albicans* and *C. glabrata* adhered cells and biofilm, and at 10 μg ml−1 against *Trichophyton rubrum (T. rubrum)*. In summary, Ag-NPs have also been revealed as potential biocide against fungal strains, and could help to prevent fungal infections for protection of human health[47].

3.4 Anticancer effects

Shahnaz Majeed et.al (2010) reported anticancer analysis (via MTT assay) efficacy of AgNPs on MCF-7 cancer cells. These AgNPs showed a concentration-dependent anticancer effect on MCF-7 cells. The IC50 value was 70 µg/ml after 24 h of incubation. Upon further incubation for 48 h, the toxicity increased and the IC50 value was 50 µg/ml,. Thus, these nanoparticles display anticancer activity against MCF-7 breast cancer cells[47].

The cytotoxicity of the AgNPs were studied in vitro against HCT-116, MCF-7, Hep-G2 and Caco-2 cancer cell lines at different concentration (0, 5, 12.5, 25, 50 µg/mL).
The results obtained from MTT assay after 48hrs of incubation showed that fruits/AgNPs showed significant effect on Hep-G2 and MCF-7 with IC50 = 17.2 and 22.4 µg respectively. Fruits/ AgNPs cytotoxic effect on HCT-116 and Caco-2 showed insignificant anticancer activity with IC_{50} > 30µg/ml.
Leaves/SNPs was effective only against Hep-G2 cancer cell line, as it led to inhibition in cell growth as concluded from IC_{50} values 10.2µg /mL
Treatment of tested cell cancer cell lines with seeds/AgNPs led to insignificant cytotoxic effect with IC_{50} values above 30 µg.
At the same time treatment of HCT-116 and Hep-G2 cancer cell lines with roots/AgNPs led to significant cytotoxic effects with IC_{50} 21.2 µg for HCT-116 and IC_{50} = 22.4 µg for Hep-G2 . Insignificant cytotoxic effect was observed on MCF-7 and Caco-2 cell lines **[48].** Thus silver nanoparticles exhibit significant anticancer effects against some human cancer cell lines**.**

CONCLUSION

The study of silver nanoparticles has emerged as a current trend due to its widespread applications. These nanoparticles have many important applications that include spectrally selective coating for solar energy absorption, as optical receptors, polarizing filters, catalysts in chemical reaction, and other biomedical applications. Thus green chemistry provides us an environment friendly, easy, cost effective and energy efficient single step technique for the synthesis of silver nanoparticles with no hazardous byproducts.

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