GREEN SYNTHESIS OF SILVER NANO PARTICLES: A REVIEW

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ABSTRACT

In recent days, green synthesis has become most efficient method for synthesis of silver nanoparticles(NP) using biological extract. Biological extract is obtained from plants, animals, insects and microorganisms. In this method, bio extracts are used as reducing agent and capping agent for synthesis of silver nanoparticles. Variation in the size and shape of the Ag-NPs plays a vital role in the antibacterial effect. The synthesis can also be done by using chemical process but the residues of this process will be harmful to the nature. The important drawback of chemical synthesis is that they use toxic substances which cause stakes to the environment. The cost to carry over the process is extremely high. The result exhibits by chemical synthesis is not effective. Green synthesis is an eco-friendly process and the result will be very much effective. They have good stability, precise dimensions and uses non-toxic safe reagents. This method is friendly in both economical and environmental phase. In this article, published information on the synthesis of Ag-NPs, properties, testing methods and its antibacterial efficacy has been summarized as review.

KEYWORDS: *Green synthesis, Ag-NPs, biological extract, antibacterial efficacy*

1.INTRODUCTION:

Nanotechnology is a technology to produce particles, molecules at nanometer with the size of 10-100nm.This method was first used by Norio Taniguchi in 1974.The properties of materials in larger size may vary from smaller size. Nano particles(NP) are classified into organic and inorganic. Inorganic involves semiconductor NPs (ZnO, ZnS), metallic NPs (Ag, Au), magnetic NPs (Fe, Co). Organic involves carbon NPs. In recent time there is a great development in gold and silver nanoparticles(NP). Silver nanoparticles(Ag-NP) shows interesting catalytic and biochemical properties which is more efficient than the bigger particles with same compositions.

There are two approaches for synthesis of Ag-NPs. Top-Down method involves splitting up of suitable bulk materials into fine particles by reducing the size of the particles with different techniques such as Pulse laser ablation, ball milling, evaporation–condensation, ball milling etc. Bottom-Up method involves synthesizing of silver nano using chemical and biological method by converting atoms into new nuclei which are further developed into particles of nano size. Top-Down method is toxic and Bottom-Up method is nontoxic (TABLE 1).

The conventional method for synthesis of silver nano is very expensive, toxic and non-environmental friendly. To overcome this scientist have identified a green route which is cost efficient, nontoxic and ecofriendly. Green synthesis is defined as production of silver nanoparticles by using biological materials such as plants, animals, bacteria, fungi which is used as a reducing agent. This method does not involve any chemicals, high pressure, high temperature as in physical and chemical method. Thus green synthesis is a great alternative for synthesis of silver nano.

TABLE 1: APPROACHES FOR SYNTHESIS OF SILVER NANO

TOP DOWN METHOD	BOTTOM UP METHOD
PHYSICAL METHODS: PULSE LASER ABLATION BALL MILLING EVAPORATION-CONDENSATION ARC DISCHARGE SPRAY PYROLYSIS PULSE WIRE DISCHARGE VAPOUR AND GAS PHASE LITHOGRAPHY	1.GREEN METHODS: EXTRACT FROM PLANTS EXTRACT FROM ANIMALS EXTRACT FROM BACTERIA EXTRACT FROM FUNGI EXTRACT FROM INSECTS EXTRACT FROM MICROORGANISM 2.CHEMICAL METHODS: CHEMICAL REDUCTION PHOTOCHEMICAL ELECTROCHEMICAL PYROLYSIS MICROWAVE SONOCHEMICAL MICROEMULSION SOLVOTHERMAL

APPLICATION OF SILVER NANO PARTICLE :

Silver nanoparticles are widely used in many applications due to their efficient and unique properties. Their performance in various fields which includes food agriculture,.

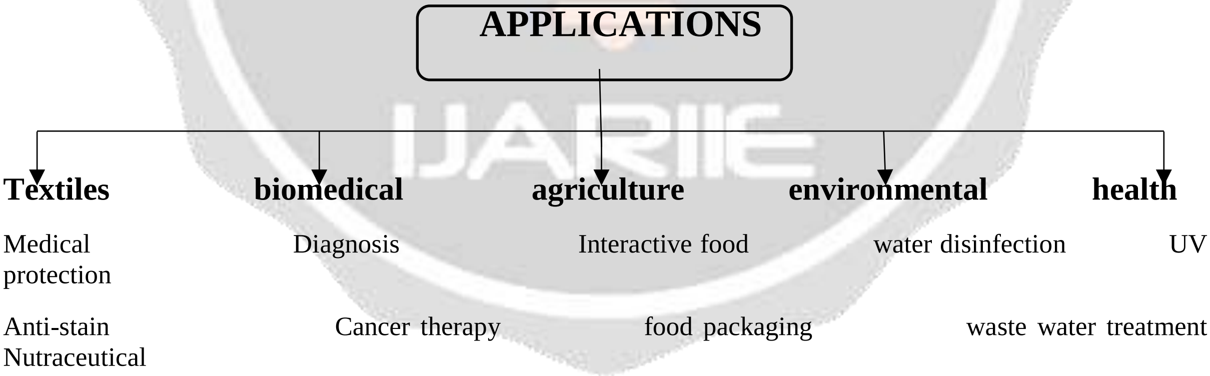


FIGURE 1: APPLICATIONS OF SILVER NANOPARTICLES [23]

medical, textiles and industrial purposes has become more effective than chemical and physical method. In the current scenario due to their excellent biological activity and non-toxicity of green synthesized Ag-NPs they are vastly used in major industries

2.GREEN SYNTHESIS:

The preliminary need for synthesis of Ag-NPs are biological extract, silver nitrate and distilled water. In order to diminish the residue toxicity level in the environment because of following typical methods, researchers have come with this emerging technique. It becomes a revolutionary one in recent period. Bio extracts are obtained from

- Plants
- Animals
- Insects
- Fungi
- Bacteria
- Algae
- Microorganisms

2.1. EXTRACT FROM PLANTS:

The extract used as a reducing agent are acquired from wide variety of plants. Various parts of plants such as roots, leaves, stems, barks, flowers, fruits and herbs are used to perform this synthesizing method. Nano particles that is synthesized using plants gives well defined shape, structure and morphology.

FIGURE 2: PROCESS SEQUENCE FOR SYNTHESIZING Ag-NPs [24]

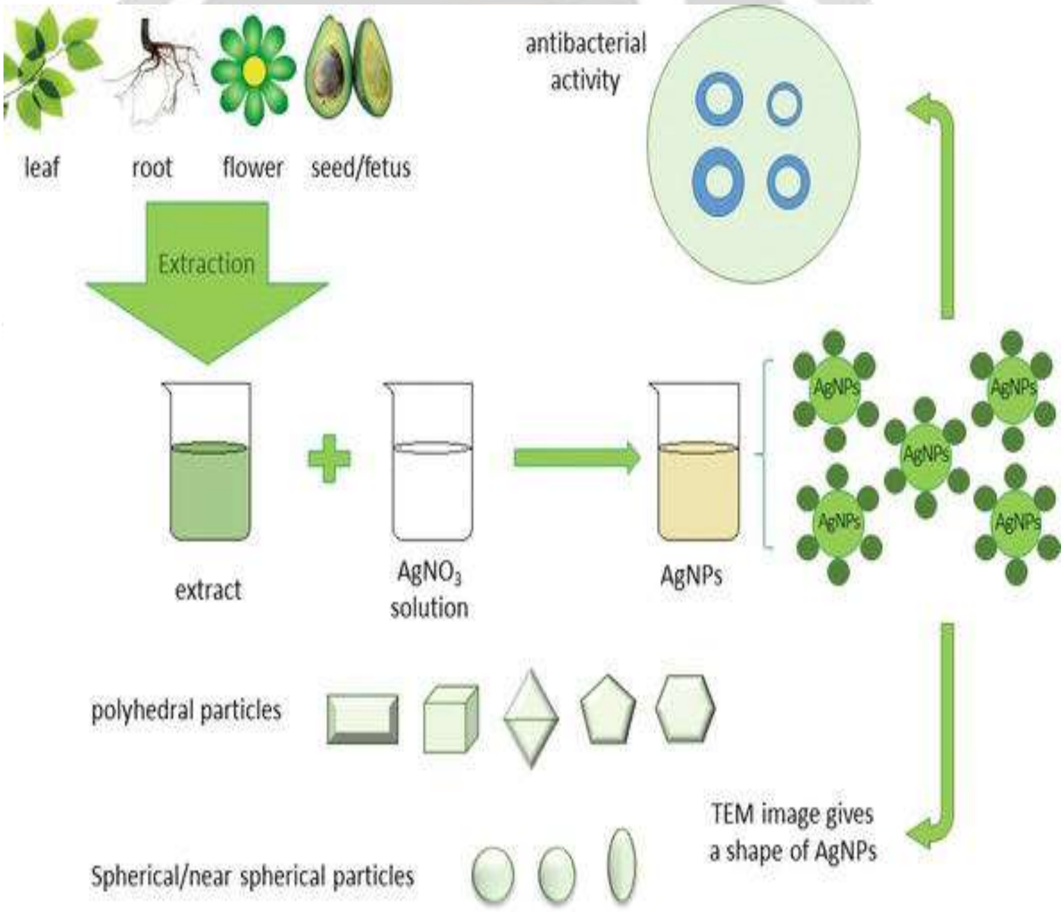


TABLE 2 : VARIOUS PLANTS USED IN PRODUCTION OF Ag-NP’S

S.NO	PLANTS COMMON NAME	BIOLOGICAL NAME	PARTS USED	REFERENCE NUMBER
1	Flinder’s rose	Capparis spinosa	Leaves	[1]
2	Lemon balm	Melissa officinalis	Leaves	[2]
3	Hemp	Cannabis sativa	Herd	[3]
4	Honey herb	Phyla dulcis	Leaves	[4]
5	Wild Gourd	Cucumis prophetaram	Leaves	[5]
6	Cinnamon	Cinnamomum zeylanicum	Barks	[6]
7	Neem tree	Azadirachta indica	Leaves	[7]
8	Japanese plum	Eriobotrya japonica	Leaves	[8]
9	Sage	Salvia spinose	Seeds	[9]
10	Olive	Olea europaea	Leaves	[10]
11	Black mustard	Brassica nigra	Seeds	[11]
12	Shepherd’ s purse	Capsella bursa-pastoris	Leaves	[11]
13	English lavender	Lavandula angustifolia	Leaves	[11]
14	Oregano	Origanum vulgare	Leaves	[11]
15	Barberry	Berberis vulgaris	Roots	[11]
16	Spanish cherry	Mimusops elengi	Leaves	[12]
17	Suj	Lysiloma acapulcensis	Stem and Root	[13]
18	Butterfly pea	Clitoria ternatea	Leaves	[14]
19	Night shade	Solanum nigrum	Leaves	[14]
20	Grape vine	Vitis vinifera	Fruit	[15]
21	Parsley	Petroselinum crispum	Leaves	[16]
22	Holy basil	Ocimium tenuiflorum	Leaves	[17]
23	Thudhuvalai	Solanum trilobatum	Leaves	[17]
24	Java plum	Syzygium cumini	Leaves	[17]
25	Gotu kola	Centella asiatica	Leaves	[17]
26	Orange	Citrus sinensis	Leaves	[17]
27	Arjuna	Terminalia arjuna	Bark	[18]
28	Banana	Musa balbisiana	Leaves	[19]
29	Guava	Psidium guajava	Leaves	[20]
30	Wood spurge	Euphorbia amygdaloides	Plant	[20]

2.2. EXTRACT FROM BACTERIA:

Bacteria is used as the reducing agent for preparation of silver nano particles. Bacterial synthesis is threatened by culture contamination, lengthy process and less control over the size of Ag-NPs. Some of the bacterium used are

- Bacillus subtillus
- Pseudomonas aeruginosa
- Bacillus brevis
- Phenerochaete chrysosporuim
- Pseudomonas putida
- Bascillus licheniformis
- Bascillus pumicus
- Streptacidiphilus durhamenis
- Deinococcus radioclurans
- Sphingomonas paucimobilis
- Escherichia coli
- Actinobacteria rhodococcussp

2.3. EXTRACT FROM FUNGI:

Extracellular synthesis of silver nano using fungi is a best alternative method due to their largescale production. Synthesis of Ag-NPs using fungi is chosen over bacteria because of their better tolerance and metal bioaccumulation property. Fungi mentioned in some of the literatures are

- Pleurotus sajor caju
- Aspergillus flavus
- Verticillium dahliae
- Aspergillus ferreus
- Penicillium oxalicum
- Penicillium citrinum
- Fusarium oxysporum
- Penicillium humicola
- Aspegillus fumigatus
- Guignardia mangifere
- Aspergillus oryzae
- White rot fungi

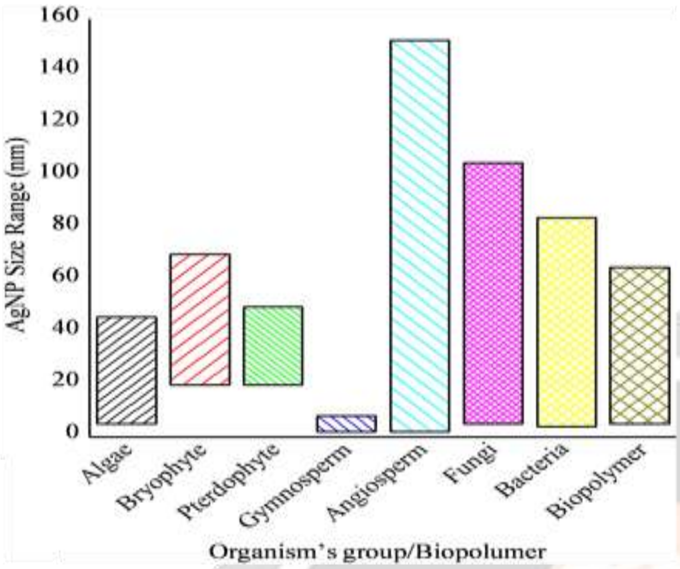
2.4. EXTRACT FROM ALGAE:

A diverse group aquatic microorganism, algae is used for the synthesis of silver nano particles. They vary in size from microscopic (Picoplankton) to macroscopic (Rhodophyta).Some of them are mentioned below.

- Padina pavonica
- Cystophora moniliformis
- Caulerpa racemose
- Turbinaria conodies
- Pithophora oedogonia
- Sargassum wightii grevilli
- Botryococcus braunii
- Caulerpa serrulate
- Sargassum myriocystum
- Desmodesmus subspicatus
- Chlorella vulgaris
- Ecklonia cava
- Padina tetrastromatica
- Gracilaria birdiae
- Acanthophora specifera
- Padina pavonica
- Spyridia fusiformis

2.5. EXTRACT FROM ANIMALS:

Animal extract are not mostly used in the synthesis of silver nano. The protein present in this biological extract is used for reducing the silver nano particles. Animal waste are mainly used in this type of synthesis which includes animal hair, bird feather, human hair. Some of them are mentioned below



- Carp fish blood
- Sheep blood serum
- Spider web

FIGURE 3: SIZE OF NANO BY VARIETY OF ORGANISM [22]

3.SYNTHESIS OF SILVER NANO:

The reducing agent for synthesizing nanoparticles will get differ according to the extract used. The synthesis of Ag-NP by biological entities is due to the presence of large number of organic chemical like carbohydrate, fat, proteins, enzymes& coenzymes, phenols flavonoids , terpenoids, alkaloids, gum, etc capable of donating electron for the reduction of Ag^{+} ions to Ag^{0}.In agglomeration the formation of assemblage will occur by increasing their size and decreasing their surface area. The stabilizer is used to avoid aggregation of formed nanoparticles.

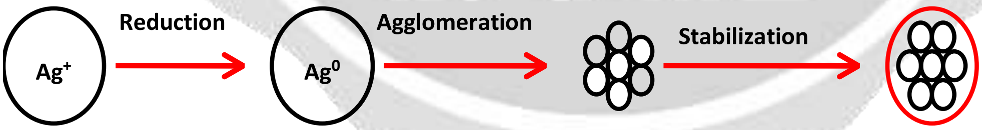


FIGURE 4: SYNTHESIS MECHANISM OF Ag-NP's [22]

3.1. POLYSACCHARIDE METHOD:

In this method, polysaccharides are used as reducing and capping agent for synthesis of silver nano particles. This reaction is performed using water which is more environmental friendly. Starch present in the solution act as reducing and capping agent which avoids the usage of chemical and toxic components. The bonding between starch and Ag-NPs are not excellent and can be overcome at high temperature which helps in the separation of synthesized particles. Thus stable Ag-NPs (10-34nm) are synthesized by autoclaving of $AgNO_3$ solution and starch (capping and reducing agent) at 15 psi and 120^0C for 5min.Another method for synthesis of Ag-NPs involves negatively charged heparin as a reducing and capping agent by heating $AgNO_3$ with heparin at 70^0C for 8hr.[21]

3.2. TOLLEN METHOD:

In this method, small sized nano particles are produced with one step process. Saccharides in the presence of ammonia are used as reducing and capping agent [$Ag(NH_3)_2$]. By products of this method are silver nano flim with particle size 50-200 nm, Ag hydrosols with particle size of 20-50 nm and Ag-NPs of different shapes. $Ag(NH_3)_2$ is a stable complex ion due to the strong affinity of ammonia with silver, therefore the concentration of ammonia and nature of reducing agent plays a major role in controlling the Ag-NPs size. Particles size lesser than 10 nm with various shapes are synthesized by changing the concentration of n-hexadecyltrimethylammonia bromide (HTAB) and tollen reagent at 120^0C.[21]

3.3. IRRADIATION METHOD:

In this method, various radiations are used for the synthesis of Ag-NPs. Laser irradiation method is applied for synthesis of Ag-NPs in the presence of Ag salt with surfactant. This produce nano particles of well defined shape and size. Laser is also implemented in the photo-sensitization technique by using benzophenone for producing nano particles. Alteration in the laser power plays a major role in the size of the particle.

$$LASER\ POWER\ \ \alpha\ \ \frac{1}{PARTICLE\ SIZE}$$

Laser power with shorter irradiation produce nano particles with ≤ 20 nm size and ≤ 5nm sized nano particles are produced at increased irradiation. In photo-sensitization method mercury lamp is also used. Microwave radiation is a another technique to produce stable Ag-NPs in the presence of carboxymethylcellulose sodium and silver nitrate solution which can withstand in room temperature for 2 months. In gamma radiolysis both silica aerogel and oligochitosan are used for synthesis of silver nano with the size of 5-15 nm at a PH of 1.8-9.0. The pulse radiolysis technique is used to study the reactions on formation of Ag-NPs.[21]

3.4.BIOLOGICAL METHOD:

Microorganism is used as a reducing and capping agent in this method for synthesis of Ag-NPs. The reducing agent involves bacteria, fungi, yeast and actinomycetes which has great potential for synthesis of Ag-NPs. This biosynthesis method is classified into two following categories,

- **Extracellular**- the reaction takes place outside the cell by reducing the inorganic components in order to obtain nano particles.
- **Intracellular**-The reaction takes place within the cell by reducing the inorganic components in order to obtain nano particles.

By having a glimpse, Bacteria Pseudomonas strutzeri produce nano particles of size 27 nm. The extracellular synthesis of silver nano using various samples in Fusarium oxysporum has been reported. The extracellular hydrogenase present in the F.oxysporum shows good redox properties and can be used as a electron shield in metal reduction. There are two steps involved in this process. Firstly, Ag^+ ions are trapped on the surface of the fungal cell. Secondly, the enzyme present inside reduces silver particles into silver nano on the surface of the fungal cell. Ag-NPs synthesized from bacterium Klebsiella pneumonia, Escherichia coli and Enterobacter cloacae are very rapid. As per many literatures Biological synthesis is majorly used method for synthesis of Ag-NPs.[21]

4. MONITORING OF SILVER NANO:

The change of color from colorless solution to yellow or brownish-yellow solution indicates the formation of Ag-NPs. The significant nano particles of size 400-450nm are indicated in SPR test. SPR is an analysis methodology used to study the molecular interactions. The UV-Vis spectral analysis indicates dependency of pH, metal ion concentration, extract content on the formation of Ag-NPs and reveal the size-stability of synthesized Ag-NPs. The SEM morphological analysis in most of the studies shows spherical shaped Ag-NPs and some literatures show irregular, triangular, hexagonal, isotropic, polyhedral, flake, flower, pentagonal, anisotropic and rod shaped structures of Ag-NPs. The XRD analysis studies the formation of Face Centered Cubic (FCC) crystalline structure, hexagonal and cubic structure. The EDS or EDAX test indicates the elemental composition in nano particles with optical absorption band peak of 3 KeV with silver weight ranging from 45 to 80%. The stability of Ag-NPs varies from 1day to 1year depending on the reducing agent and other operating process.[22]

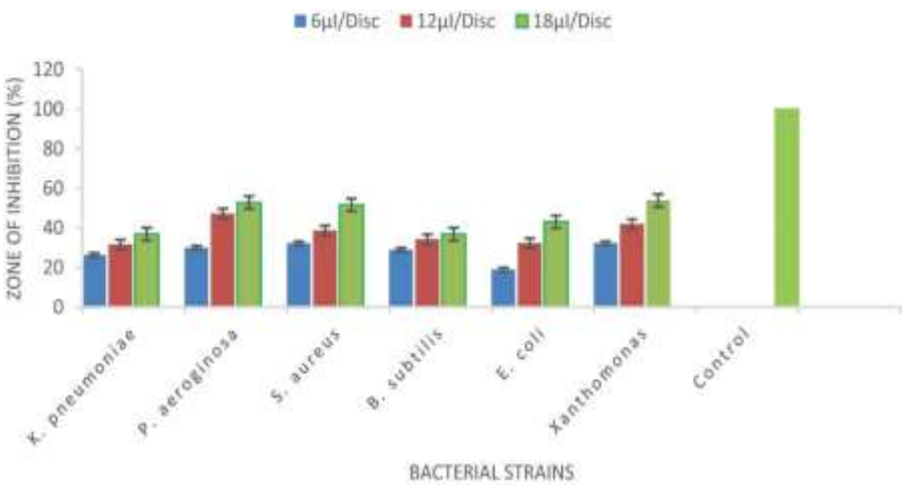


FIGURE 5: VARIOUS SHAPES OF Ag-NPs[22]

7.ANTIBACTERIAL ACTIVITY:

The antibacterial activity of gram positive and gram negative bacteria are not same but competes one another. In some literatures gram positive bacteria are more sensitive and vice versa. There are many conflicting information regarding both gram negative and gram positive bacteria. Antibacterial activity depends on the different structural characteristics of bacteria, size and shape of Ag-NPs, bacterial inoculum size, nutrition medium and exposure medium during antibacterial analysis. The antibacterial action of Ag-NPs are classified into two categories such as inhibitory action and bactericidal action. In inhibitory action bacterial cells are not killed but prevents the multiplication of bacteria. In bactericidal action bacterial cells are completely destroyed. The inhibitory method becomes bactericidal method by increasing the concentration of Ag-NPs. In the bactericidal method, the Ag^+ ions are released which act as a reservoirs for antibacterial activity.

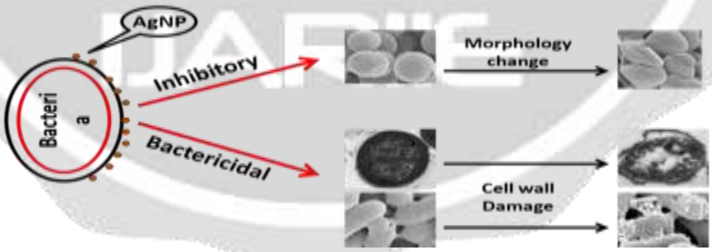


FIGURE 6: ACTIVITY OF SILVER NANO ON BACTERIA [22]

Zone of inhibition is the circular area where the bacterial cells do not grow. Zone of inhibition increases with increases in the antibacterial efficacy of silver nano.

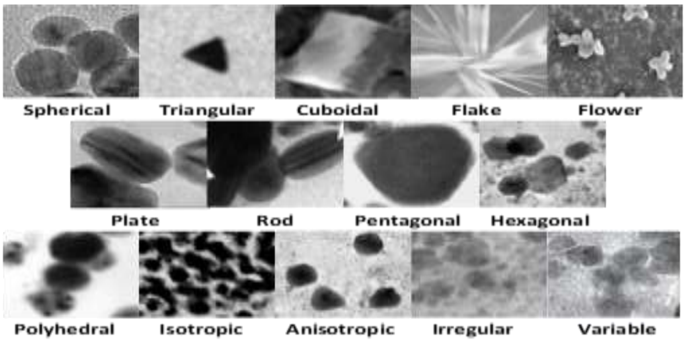


FIGURE 7: ANTIBACTERIAL ACTIVITY OF DIFFERENT BACTERIA[25]

8.CONCLUSION:

Green synthesis of silver nano using green route has been available in many literatures. Organisms ranging from straightforward bacteria to highly complex eukaryotes can be used in the synthesis of Ag-NPs of various size and shape. Various methodology and technique has been used in the synthesis and analysis of silver nano particles. However, the synthesis of silver nano particles in high yield and wide range of shapes are difficult. In the production of Ag-NPs ,using plants has advantages compared to other biological entities which can overcome the slow route of using microorganism and sustain their culture which can lose their potential toward synthesis of Ag-NPs. Thus green route for synthesis of silver nano avoids usage of chemicals and cost efficient. Ag-NPs emerged in present and future era, with wide variety of applications such as incorporating cardiovascular implants, dentistry, medicine, therapeutics, biosensors, agriculture, and many more.

REFERENCES:

1. Benakashani, F., Allafchian, A. R., & Jalali, S. A. H. (2016). Biosynthesis of silver nanoparticles using Capparis spinosa L. leaf extract and their antibacterial activity. *Karbala International Journal of Modern Science*, *2*(4), 251-258.
2. de Jesús Ruíz-Baltazar, Á., Reyes-López, S. Y., Larrañaga, D., Estévez, M., & Pérez, R. (2017). Green synthesis of silver nanoparticles using a Melissa officinalis leaf extract with antibacterial properties. *Results in physics*, *7*, 2639-2643.
3. Mandal, S., Marpu, S. B., Hughes, R., Omary, M. A., & Shi, S. Q. (2021). Green synthesis of silver nanoparticles using Cannabis sativa extracts and their anti-bacterial activity. *Green and Sustainable Chemistry*, *11*(1), 38-48.
4. Carson, L., Bandara, S., Joseph, M., Green, T., Grady, T., Osuji, G., ... & Woldesenbet, S. (2020). Green synthesis of silver nanoparticles with antimicrobial properties using Phyla dulcis plant extract. *Foodborne Pathogens and Disease*, *17*(8), 504-511.
5. Hemlata, P. R. M., Singh, A. P., & Tejavath, K. K. (2020). Biosynthesis of silver nanoparticles using cucumis prophetarum aqueous leaf extract and their antibacterial and antiproliferative activity against cancer cell lines. *ACS omega*, *5*(10), 5520.
6. Satishkumar, M., Sneha, K., Won, S. W., Cho, C. W., Kim, S., & Yun, Y. S. (2009). Cinnamon zeylanicum bark extract and powder mediated green synthesis of nano-crystalline silver particles and its antibacterial activity. *Colloids Surf. B: Biointerface*, *73*, 332-338.
7. Roy, P., Das, B., Mohanty, A., & Mohapatra, S. (2017). Green synthesis of silver nanoparticles using Azadirachta indica leaf extract and its antimicrobial study. *Applied Nanoscience*, *7*(8), 843-850.
8. Rao, B., & Tang, R. C. (2017). Green synthesis of silver nanoparticles with antibacterial activities using aqueous Eriobotrya japonica leaf extract. *Advances in natural sciences: Nanoscience and nanotechnology*, *8*(1), 015014.
9. Corrêa, M. G., Pires, P. R., Ribeiro, F. V., Pimentel, S. Z., Casarin, R. C. V., Cirano, F. R., ... & Casati, M. Z. (2017). Systemic treatment with resveratrol and/or curcumin reduces the progression of experimental periodontitis in rats. *Journal of periodontal research*, *52*(2), 201-209.
10. Khalil, M. M. H., Ismail, E. H., El-Baghdady, K. Z., & Mohamed, D. (2014). Green synthesis of silver nanoparticles using olive leaf extract and its antibacterial activity. Arab J Chem 7 (6): 1131–1139.

11. Atalar, M. N., Baran, A., Baran, M. F., Keskin, C., Aktepe, N., Yavuz, Ö., & İrtegun Kandemir, S. (2021). Economic fast synthesis of olive leaf extract and silver nanoparticles and biomedical applications. *Particulate Science and Technology*, 1-9.
12. Prakash, P., Gnanaprakasam, P., Emmanuel, R., Arokiyaraj, S., & Saravanan, M. (2013). Green synthesis of silver nanoparticles from leaf extract of Mimusops elengi, Linn. for enhanced antibacterial activity against multi drug resistant clinical isolates. *Colloids and Surfaces B: Biointerfaces*, *108*, 255-259.
13. Korkmaz, N., Ceylan, Y., Hamid, A., Karadağ, A., Bülbül, A. S., Aftab, M. N., ... & Şen, F. (2020). Biogenic silver nanoparticles synthesized via Mimusops elengi fruit extract, a study on antibiofilm, antibacterial, and anticancer activities. *Journal of Drug Delivery Science and Technology*, *59*, 101864.
14. Krithiga, N., Rajalakshmi, A., & Jayachitra, A. (2015). Green synthesis of silver nanoparticles using leaf extracts of Clitoria ternatea and Solanum nigrum and study of its antibacterial effect against common nosocomial pathogens. *Journal of Nanoscience*, *2015*.
15. Gnanajobitha, G., Paulkumar, K., Vanaja, M., Rajeshkumar, S., Malarkodi, C., Annadurai, G., & Kannan, C. (2013). Fruit-mediated synthesis of silver nanoparticles using Vitis vinifera and evaluation of their antimicrobial efficacy. *Journal of Nanostructure in Chemistry*, *3*(1), 1-6.
16. Roy, K., Sarkar, C. K., & Ghosh, C. K. (2015). Plant-mediated synthesis of silver nanoparticles using parsley (Petroselinum crispum) leaf extract: spectral analysis of the particles and antibacterial study. *Applied Nanoscience*, *5*(8), 945-951.
17. Logeswari, P., Silambarasan, S., & Abraham, J. (2015). Synthesis of silver nanoparticles using plants extract and analysis of their antimicrobial property. J Saudi Chem Soc 19: 311–317.
18. Sudarsan, S., Kumar Shankar, M., Kumar Belagal Motatis, A., Shankar, S., Krishnappa, D., Mohan, C. D., ... & Siddaiah, C. N. (2021). Green synthesis of silver nanoparticles by Cytobacillus firmus isolated from the stem bark of Terminalia arjuna and their antimicrobial activity. *Biomolecules*, *11*(2), 259.
19. Banerjee, P., Satapathy, M., Mukhopahayay, A., & Das, P. (2014). Leaf extract mediated green synthesis of silver nanoparticles from widely available Indian plants: synthesis, characterization, antimicrobial property and toxicity analysis. *Bioresources and Bioprocessing*, *1*(1), 1-10.
20. Diamond, D. M., Campbell, A. M., Park, C. R., Halonen, J., & Zoladz, P. R. (2007). The temporal dynamics model of emotional memory processing: a synthesis on the neurobiological basis of stress-induced amnesia, flashbulb and traumatic memories, and the Yerkes-Dodson law. *Neural plasticity*, *2007*.
21. Kaler, A., Patel, N., & Banerjee, U. C. (2010). Green synthesis of silver nanoparticles. *Curr Res Inf Pharm Sci*, *11*(4), 68-71.
22. Srikar, S. K., Giri, D. D., Pal, D. B., Mishra, P. K., & Upadhyay, S. N. (2016). Green synthesis of silver nanoparticles: a review, Green Sustain. Chem. 6 (2016) 34–56.
23. Keat, C. L., Aziz, A., Eid, A. M., & Elmarzugi, N. A. (2015). Biosynthesis of nanoparticles and silver nanoparticles. *Bioresources and Bioprocessing*, *2*(1), 1-11.
24. Bedlovicová, Z., & Salayová, A. (2017). Green-Synthesized Silver Nanoparticles and Their Potential for Antibacterial Applications. *Bacterial Pathogenesis and Antibacterial Control*.
25. Uz-Zaman, K., Bakht, J., Malikovna, B. K., Elsharkawy, E. R., Khalil, A. A., Bawazeer, S., & Rauf, A. (2020). Trillium govanianum Wall. Ex. Royle rhizomes extract-medicated silver nanoparticles and their antimicrobial activity. *Green Processing and Synthesis*, *9*(1), 503-514.