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Silver Nanoparticles: Synthesis and Applications (Review)

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Abstract
Silver nanoparticles have been drawn the attention of the scientists due to its distinct properties particularly size dependent optical and catalytic properties, antimicrobial and electrical properties. Till today, silver nanoparticles are produced by three methods-physical, chemical and biological. Each method has its own features, merits and demerits and in this review paper each method is elaborately illustrated. The potentiality of silver nanoparticles in the waste water treatment and antimicrobial activities is thoroughly discussed. In addition, mechanism of degradation of organic pollutants and antimicrobial activities of silver nanoparticles are also explained with figure.
Keywords*: Silver nanoparticles, catalytic, dye, antimicrobial activity, pollutants.*

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I. Introduction

Nanotechnology, which is a emerging field in the contemporary era, has drawn the attention of the researcher in order to design, synthesis and modification of particles of 1 to 100nm size which show unique properties such as large surface area to volume ratio, chemical, optical, mechanical and electrical properties. [1] Due to the unique properties of nanomaterials, it is widely used in various fields such as environmental, textile, healthcare, electrical, biotechnological etc.. [2]Over the last decades, many efforts have been carried out to invent a process of simple, economically feasible, eco-friendly and rapid for the production of nanoparticles of desired size and shape.

Generally physical, chemical and biological methods are used for the synthesis of nanomaterials. Each method has its own pros and cons with respect to various parameters of process. For example, biological method is simple, ecofriendly whereas chemical method is not eco-friendly but feasible for large scale production. [3-5] Different nanomaterials such as metallic, metal oxide, organic etc are fabricated extensively over the last two decades due to the fact that these nanomaterials have application in various industries. Among these nanomaterials, silver is the most promising nanomaterials because of its unique optical,electrical and chemical properties. It is used in pharmaceutical industry, textile industry, cosmetic industry, electronics etc.[6-7]

Silver nanomaterials have been also synthesized by physical, chemical and biological methods. AgNPS synthesized by chemical methods are unstable and due to overcome this problem stabilizing agent are used along with reducing agent in the chemical reduction method. In case of biological method, biomolecule act as both reducing and stabilizing agent.[10] In this review, various methods of silver nanoparticle synthesis is illustrated elaborately. In addition, antimicrobial activites and environmental application of silver nanoparticles are also explained.

Synthesis of Silver Nanoparticles

Silver nanoparticles are synthesized by physical, chemical and biological method. Physical methods include evaporation and condensation and laser ablation while chemical methods include chemical reduction, microemulsion, UV-initiated irradiation, photoinduced reduction, electrochemical synthetic method and microwave assisted method. In biological method microbes such as bacteria, fungi, algae and plant extract are used. In the table -1, various methods of silver nanoparticle synthesis are outlined.

Table-1" various methods of silver nanoparticle synthesis

Synthesis Methods		
Physical Method	Chemical Method	Biological Method
1.Evaporation and condensation 2.Pulse laser ablation	1.Chemical reduction, 2.Microemulsion, 3.UV-initiated irradiation,	1.Microbial Method a)Bacteria b)Fungi

	4.Photoinduced reduction, 5.Electrochemical synthetic method 6.Microwave assisted method	c) algae 2.Plant extract

Physical Methods
Evaporation and condensation method

The evaporation and condensation method consists of two steps-evaporation of silver source materials followed by cooling of produced silver nanaparticle. For instances, Jung et.al., fabricated silver nanoparticles using a small ceramic heater[11]. This method is costly because larger amount of energy is required in this process and there is a need of special cooling system for cooling the evaporated vapor at a suitable rate. [12-13]

Pulse ablation method

Pulse laser ablation method is used to synthesis Ag nanoparticles. [14-18] The main merit of this process is that pure silver nanoparticles is produced from this method because no chemical reagent is used in this process.[19] In addition, the efficiency of this process depends on wavelength of laser, duration of laser pulses, duration of ablation time and the medium.[20-23] Tsuji et.al., synthesized silver nanoparticle of 20-50nm was synthesized by laser ablation method using water as medium and laser ablation of wavelength 800nm. [24]

Chemical Method
Chemical reduction

Chemical reduction method is mostly used method for the synthesis of silver nanoparticles. In this method, organic and inorganic reducing agents are used for the reduction of silver ion in aqueous and non aqueous solution into silver nanoparticles.[25-27] The most commonly used reducing agents are sodium citrate, ascorbate, sodium borohydride ($NaBH_4$), elemental hydrogen, polyol process,Tollens reagent, N, N-dimethylformamide (DMF), and poly (ethylene glycol)-block copolymers.

The drawback of this process is instability of the produced silver nanoparticles or the agglomeration of silver nanoparticles. [25-27] For improving stability of silver nanoparticles or avoiding agglomeration problems some stabilizing agents are used. Polymeric compounds such as poly (vinyl alcohol), poly (vinylpyrrolidone), poly (ethylene glycol), poly (methacrylic acid), and polymethylmethacrylate have been reported to be the effective protective agents to stabilize silver NPs.

Mavani et.al., synthesized silver nanoparticles by the chemical reduction of silver nitrate by the sodium borohydride in the presence of polyvinylpyrrolidone. Here, sodium borohydride acted as reducing agent and polyvinylpyrrolidone acted as stabilizing agent.[27]

Microemulsion method

Microemulsion method is used for the fabrication of uniformed sized nanoparticles. In this method, nanoparticle is synthesized in two phase organic and inorganic system. Intially, partial separation of reactants (metal precursor and reducing agent) occurs in two immiscible phase. Stable nanomaterial is produced at the interface of the system because synthesized nanomaterial is coated with stabilizer.[28] For example, Chharate et.al., synthesized siler nanoparticle by microemulsion method. In that synthesis procedure, silver nitrate, sodium borohydride, hepatne-water were used as metal precursor, reducing agent and two phase system respectively. [29]The primary drawback of the system is the use of toxic organic solvent.

UV Initiated Photoreduction

UV initiated photoreduction is a simple and effective method for the fabrication of silver nanoparticles in the presence of a suitable stabilizing agent. For instance, Huang and Yang synthesized silver nanoparticles via UV initiated photoreduction method in the presence of stabilized agent clay. During the synthesis Huang and Yang also experimented the effect of duration of UV irradiation on the size of silver nanoparticles and found that higher the duration time the smaller the size of silver nanoparticles was.[30]

Photoinduced Reduction

Photoinduced or photocatalytic synthesis is another method of fabrication of silver nanoparticles. This method is regarded as a clean, convenient and versatile method. For example, 8nm silver nanoparticle was produced by photoinduced reduction method using poly (styrene sulfonate)/poly (allylamine hydrochloride) polyelectrolyte capsules as microreactors[31].

Electrochemical Synthetic Method

Silver nanoparticle was also synthesized by electrochemical method. In this method, particles size was controlled by optimizing the electrolysis parameter. Moreover, homogeneity of nanoparticles was also adjusted by changing the concentration of electrolytic solution. For example, Polyphenylpyrrole coated silver nanospheroids (3-20 nm) were fabricated by electrochemical reduction at the liquid/liquid interface. In this method, silver metal ion was transferred from aqueous phase to organic phase, where it reacted with pyrrole monomer [32].

Microwave Assisted Method

Microwave assisted method is considered as potential method for the synthesis of silver nanoparticles because it yields nanomaterials of higher crystallinity, narrower size distribution.[33] The key benefits of this methods are shorter reaction time, less production of chemical waste and higher yields.[33-34] For example, Chen et.al., synthesized silver nanoparticle using carboxymethyl cellulose as reducing and stabilizing agent through microwave synthesis method. It was also found that the particle size of silver material depended on concentration of both carboxymethyl cellulose and silver nitrate. [35]

Biological Methods

Microbial synthesis method

Microbial Synthesis method is regarded as one of the potential methods for the fabrication of silver nanoparticles. In this method, biomolecules that are metabolite of microorganism such as bacteria, fungi and algae act as both reducing and stabilizing agent during the synthesis of silver nanoparticles by microbial method. In the microbial production of silver nanoparticles, bacteria and fungi are generally frequently used as a source of biomolecules. There are three steps involving in this method and these are culturing of microorganism, separation of cell free metabolite and reduction of metal ions. In the table-2, synthesis of silver nanoparticles by microbial method is listed.

Bacteria

Silver nanoparticles were synthesized by both intracellular and extracellular approaches by bacteria. In intracellular method, metal ions(Ag^+) transported to the bacteria cell wall due to the electrostatic attraction and on the bacteria cell wall metal ions reduced to the metal (Ag^+) nanoparticles by the enzyme of that cell wall. However, In the extracellular method, reduction of metal ions occurs outside the bacteria cell wall and reductase come out from the bacteria cell. [36] Between these two methods, recovery of metal nanoparticle is simple in extracellular method.For example, Gurunathan et.al., synthesized silver nanoparticles by extracellular method using the supernatant of E.Coli.[37] In another study, Sriram et.al., fabricated silver nanoparticles by intracellular method using Bacillus licheniformis.[38]

Fungi

Silver nanoparticles were also fabricated using fungi by both intracellular and extracellular methods as like as bacteria.[39-40] The merits of these process are cost effective and do not require any specific conditions like high pressure, energy and temperature.[41] Rose et al., synthesized silver nanoparticles at neutral pH and 60 °C using *Penicillium oxalicum* as fungal stain and 15 mM silver nitrate as metal precursor.[42]

Algae

Like bacteria and fungi, both intracellular and extracellular methods are thoroughly used for the synthesis of silver nanoparticles using alage. The algal extract,reductase plays a vital role in the reduction of metal ions. The main advantages of this method is very small amounts of time is required for the fabrication of silver nanomaterials. For example. Sinha et.al., synthesis silver nanoparticles of 34nm within in few minutes after mixing of algal extract (*Pithophora oedogonia*) and metal precursor.[43]

Table-2: Microbial synthesis of silver nanoparticles.

Microorganism	Size(nm)	Shape	References
Caulerpa scalpelliformis	16-47	Spherical	[44]
Penicillum italicum	33		[45]
Phomopsis liquidambaris	18.7	Spherical	[46]
Botryosphaeria rhodina	2-50	Spherical	[47]
Candida glabrata	2-15	Spherical	[48]
Ulva fasciata	4-18	Spherical	[49]
Padina pavonica	20-70	Spherical	[50]
Chlorella ellipsoidea		Spherical	[51]
Gelidium amansii	27-54	Spherical	[52]

Plant mediated synthesis

Plant mediated synthesis of silver nanoparticles is a rapid, ecofriendly,non-pathogenic, economically feasible, single step process. In this process, biomolecules such as proteins, amino acids, enzymes, polysaccharides, alkaloids, tannins, phenolics, saponins, terpinoids and vitamins that are obtained from the extraction of various parts of the plant act as both reducing agent and stabilizing agent. This method has three steps. Firstly, parts of plant are collected and washed. Secondly, extraction of biomolecules from various plants using either organic or inorganic solvent . Finally, metal precursor was reduced to metal nanoparticles by treating metal precursor with biomolecules. For example, from the literature survey it has been found that silver nanoparticles was synthesized using various parts of various plants. In the table-3,plant mediated synthesis of silver nanoparticles are listed.

Table-3: Plant mediated synthesis of silver nanoparticles.

Plant	Size(nm)	Shape	References
Alternanthera dentate (Leaves)	50–100	Spherical	[53]
Acorus calamus (Rhizome)	31.83	Spherical	[54]
Boerhaavia diffusa (Whole plant)	25	Spherical	[55]
Tea extract (Leaves)	20-90	Spherical	[56]
Tribulus terrestris (Fruit)	16-28	Spherical	[57]
Cocous nucifera	22	Spherical	[58]
Abutilon indicum (Leaves)	7-17	Spherical	[59]
Pistacia atlantica (Seeds)	10-50	Spherical	[60]
Ziziphora tenuior (Leaves)	8-40	Spherical	[61]
Ficus carica	13	Spherical	[62]

Applications of Silver nanoparticles
Environmental Application

Silver nanoparticles are considered as a potential materials in the waste water treatment branch and for this reason it is frequently used for the remediation of recalcitrant organic dyes, pesticides, antibiotics, heavy metals from waste water under sunlight. In the presence of sunlight, upon the absorption of solar radiation, valence electron of silver excited to the higher energy state and this electron adsorbed by the oxygen and hydroxyl group resulting in the formation of radicals which degrade the organic compounds(dyes, pesticides, antibiotics etc.) that adsorbed on silver nanoparticle surface. In addition, the hole created on the silver nanoparticles accept electron from dye resulting in the degradation of organic compounds.[63]

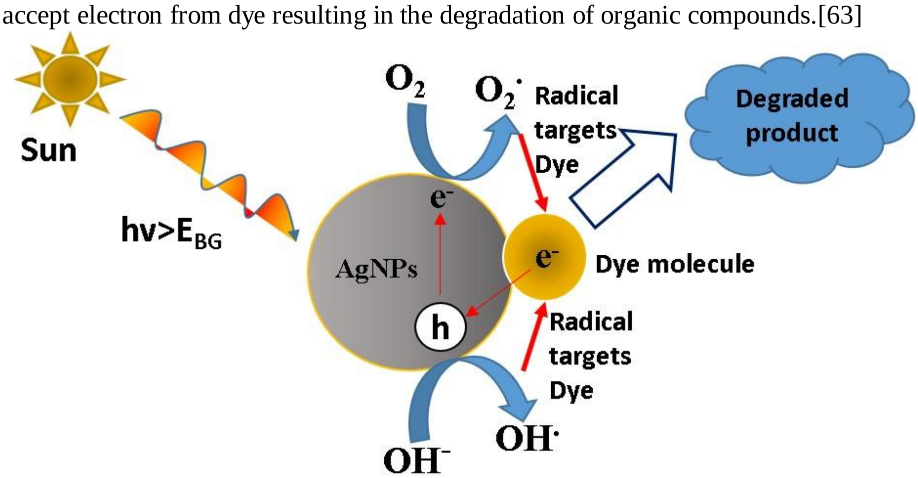

Figure-1: Dye degradation mechanism of silver nanoparticles.[63]

For example, Saha et.al. synthesized silver nanoparticles(8-32nm) via green method and evaluated its photodegradation performance against methylene blue. It has been found that within 10 min 100% methylene blue dye degraded in the presence of silver nanoparticle. [64].

In another study, Allam et.al., fabricated silver nanoparticles via microbial method and investigated its photo degradation efficiency against dye and it was observed that 97% dye degraded by silver nanoparticles.[65]

Antimicrobial Activity

Silver nanoparticle is considered as a potential antimicrobial agents against a wide range of microorganism such as bacteria, fungi and viruses etc. Still now the exact mechanism of antimicrobial activities of silver is not clear. From the survey of literature it has been found that silver nanoparticles enter into the bacteria cell membrane, and causes various malfunctioning in the cell, such as ribosomal,enzymes, protein and DNA destabilization, ROS generation,DNA damage, leading to complete cell death.[66-68].In addition, the antimicrobial properties of silver nanoparticles varies with its size, shape and its surround environment such as pH,ionic strength. For example. The spherical shaped silver nanoparticles exhibited lower minimum inhibitory concentration value (190–195 μg/ml) than that of rod shaped nanoparticles (340–358 μg/ml) against bacteria such as *E. coli*.[69]

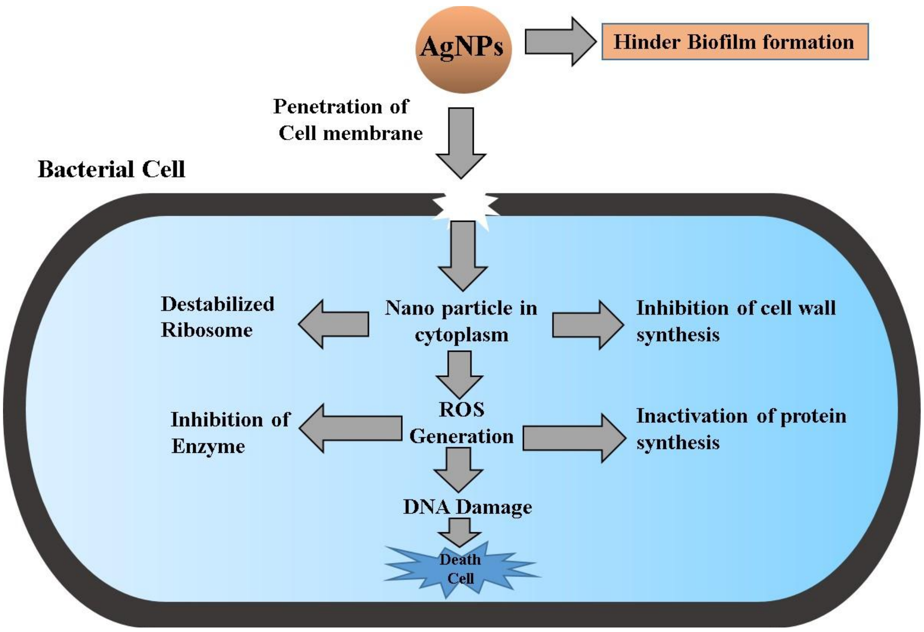

Figure-2: Antimicrobial mechanism of silver nanoparticles. [66-68]

II. Conclusion

Silver nanoparticles is synthesized through various routes such as physical, chemical and green methods that are outlined elaborately in this review paper. Among these methods, biological methods for silver nanoparticle synthesis is simple, rapid, cost effective, environmentally benign and energy efficient. In addition, although chemical methods for silver nanoparticle fabrication has several advantages over other methods, it is toxic and not environmental friendly. In this review paper, potentiality of silver nanoparticles as adsorbent or catalyst in the removal of pollutants from waste water and as microbial agents are throuoghly discussed with illustrating the basic mechanism for antimicrobial activities. Nowadays, researchers are working on the development of biological methods for the synthesis of silver nanoparticles so that in the nearest future silver nanoparticle can be fabricated on large scale by biological method.

Conflict of interest

Authors declare that there is no conflict of interest**.**

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