Green Synthesis of Silver Nanoparticles–Review of Biosynthetic Techniques

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Abstract: Nanoscience research has gained prominence in recent years owing to their diverse applications in wide-ranging fields. Consequently, the syntheses of the nanoparticles have also gained attention and many different methods have been reported in literature. In an attempt to address environmental concerns, biosynthesis of nanoparticles has been attempted using different techniques. Silver nanoparticles has been one of the most promising amongst all nanoparticles studied this far and have therefore been the subject of a large number of research publications. This review gives an insight into the 'Green" synthesis of silver nanoparticles and discusses the merits and demerits of each such technique. In addition, it also discusses the factors affecting the synthetic processes.

Index Terms: Nanoscience, Ag nanoparticles, Green synthesis, Plant extracts, Capping and Stabilizing agent,Bioefficacy

1. INTRODUCTION

Today, nanoscience is one of the most active areas of research in diverse fields such as medicine [1], material science [2] and engineering [3]. This is due to the fact that nanoparticles have novel properties such as catalytic activity [4], thermal and electrical conductivity [1a], optical absorptivity and biological applications [5] all of which are primarily due to their large surface area to volume ratio. The synthesis of nanoparticles may be done either by physical or chemical methods which include methods such as evaporation-condensation using ceramic heater, tube furnace [6], laser ablation [7][8], chemical reduction using either inorganic or organic reducing agents [9] , electrochemical methods [10] , photochemical reduction [11] , gamma irradiation and electron irradiation [12] , microwave processing [13] , thermal decomposition of silver oxalate in water or in ethylene glycol [12] , microemulsion [14] and biological synthesis [15]. However, the chemical synthesis of nanoparticles has several occupational hazards on prolonged exposure such as carcinogenicity, genotoxicity, cytotoxicity and general toxicity [16]. Thus, the synthesis of nanoparticles using green sources is a newly developing alternative.

Due to growing concerns with respect to the environment, 'green chemistry' is a very popular field. The concept is implemented in nanoparticle synthesis with the use of natural resources like fungi, bacteria and plants as starting materials. Although it is a comparatively newer and underdeveloped field, it has gained considerable interest owing to fact that the process is nontoxic and safe with minimal pollution risk, economical and cost-effective as there is an abundance of raw materials [17]. Moreover, they have a wide range of biological activity, like antimicrobial [18], anticancer [1c], and anti-inflammatory [19]. Silver nanoparticles especially have been known to possess antibacterial [20], antifungal [21] and antioxidant properties [22]. Although many of the nanoparticles synthesized so far have been found to possess catalytic properties, no specific reaction is hitherto known where the Ag nps may have been specifically used as a catalyst [23].

1.0 Biological Sources of Silver Nanoparticles

Nanoparticles synthesized by biological methods have been found to be pharmacologically more active than those prepared by physico-chemical techniques. Biosynthesis of nanoparticles particularly from medicinal plants have been found to be the most bioactive. This is possibly due to the attachment of pharmacologically active phytoconstituents onto the nanoparticles during the synthesis process [24].

1.1 Using bacteria as a medium

Some Gram-negative bacteria, like Escherichia coli 013, Pseudomonas aeruginosa CCM 3955 and E. coli CCM 3954 develop resistance to silver on prolonged exposure [25,26] and in turn accumulate silver in their cell wall, amounting to as much as 25% of their dry weight. Depending on the type of "broth" that is used during the incubation of the bacteria, extracellular or intracellular synthesis may be promoted [19] This provides a selection which makes the process of synthesis by the use of bacteria a flexible and inexpensive method. However, bacteria as a source of silver nanoparticles pose a few drawbacks. The rate of synthesis is quite slow and the number of sizes and shapes that are available is also limited [27]. Most importantly, cultures of bacteria may not always be safe to handle and therefore it cannot be termed as an efficient method of synthesis particularly from the industry perspective.

1.2 Using fungi as a medium

Fungi are a viable source of silver nanoparticles due to their tolerance and metal bioaccumulation ability, high binding capacity, and intracellular uptake [19, 28]. They are much simpler to handle at the bench scale than bacteria. The enzymes secreted by them help reduce silver ions facilitating the formation of nanoparticles [16,19]

1.3 Using plants as a medium

Many of the plants which are used in the biosynthesis of silver nanoparticles, such as neem, tulsi, etc. also have pronounced

medicinal properties, like antibacterial [20], antifungal [21] , anti-inflammatory [19] and anti-cancer [21] properties. These effects have been found to be enhanced when nanoparticles are synthesized using these plant extracts. Moreover, plants are easily available and easier and safer to handle. The synthetic process involving plant extracts is also simple and fast, unlike in bacteria and fungi, which require either multi-step or very complex procedures [15, 29, 30]. Plants have a variety of biomolecules such as enzymes, proteins, amino acids, vitamins, polysaccharides and organic acids all of which aid in bio-reduction during the synthesis of metal nanoparticles. In addition, they also act as capping and stabilizing agents and help prevent agglomeration. They are able to reduce the metal ions faster than either fungi or bacteria. Of the various biologically synthesized nanoparticles known so far, those using medicinal plants have been found to be the most pharmacologically active possibly due to the attachment of the pharmacologically active residues.

For the synthesis of nanoparticles using plant extracts, the plant parts, which may be root, leaf, bark, or any other, are washed thoroughly with distilled water, cut into small pieces and boiled for extraction. The extract is then purified by filtration and centrifugation. Depending on the species of the plant, different ratios of plant extract, metal salt solution and water are used for the synthesis. Incubation is done to reduce the metal salt, followed by repeated cycles of ultrasonication, washing, and centrifugation to remove the biomass. These steps allow for the cell wall to be broken down to release the nanoparticles. This is followed by further centrifugation, washing with de-ionised water or ethanol and finally collection in the form of a fine powder. Good mono-dispersity i.e., a narrow size distribution can be achieved by controlling the relevant critical parameters, like incubation period, mixing ratio, temperature, pH, and aeration. The mechanism underlying the biological synthesis of nanoparticles is not yet fully understood, except that it depends on the species and different phytochemical components of the plants used for synthesis. The characteristic colour change for the presence of silver nanoparticles is from yellow to brown. This occurs due to surface plasmon vibration [31,32]. This colour change is the first qualitative indication for the synthesis of nanoparticles. Further characterization is then done by methods like UV-visible spectroscopy, XRD, FTIR analysis, SEM/EDS, FESEM, and TEM.

Silver exists in its +1oxidation state in silver salts such as nitrates which must be reduced to silver in the 0 oxidation state to form nanoparticles which at times make use of toxic chemicals. Using plant extracts removes this step as the reduction involves biomolecules which involve zero toxicity. Several biomolecules like phenolics, terpenoids, polysaccharides, flavones, alkaloids, proteins, enzymes, amino acids, and alcoholic compounds may be responsible for the same [19]. The -NH_2 or -OH groups of alcohols or phenols and aromatic >C=C< groups of proteins were found to be responsible for the reduction of silver nitrate into silver nanoparticles [33] . Silver nitrate first gets ionised into Ag^+ and NO_3^- ions. The Ag^+ ions are then bioreduced to Ag^0, which on nucleation followed bystabilisation form the nanoparticles.

$AgNO_3 \rightarrow Ag^+ + NO_3^-$; $Ag^+ \rightarrow Ag^0$; $Ag^0 \rightarrow$ Ag nps

For optimum energy efficiency, synthesis must be carried out as close to ambient temperature, pressure and under neutral pH conditions.

1.3.1 Factors affecting the synthesis of silver nanoparticles

Effect of pH: At lower pH (acidic environment), the nanoparticles formed were larger as compared to those formed at higher pH (basic environment), which were found to be smaller and highly dispersed [34], **Fig 1,** and therefore favoured. At lower pH, aggregation supersedes nucleation forming larger nanoparticles. However, under alkaline conditions, a larger number of functional groups become available for binding of Ag^+ ions facilitating the formation of nanoparticles with smaller diameters [18]. It has been reported that at pH 6.0, distribution of size of the obtained nanoparticles is very narrow, while at pH 7.0 it is very wide. From pH 7.0 to 11.0 range, the size distribution got narrower, and thus the polydispersity of the colloid decreased. Several other studies on effect of pH conditions havealso shown that nanoparticle formation is suppressed under acidic conditions and enhanced under basic conditions [35].

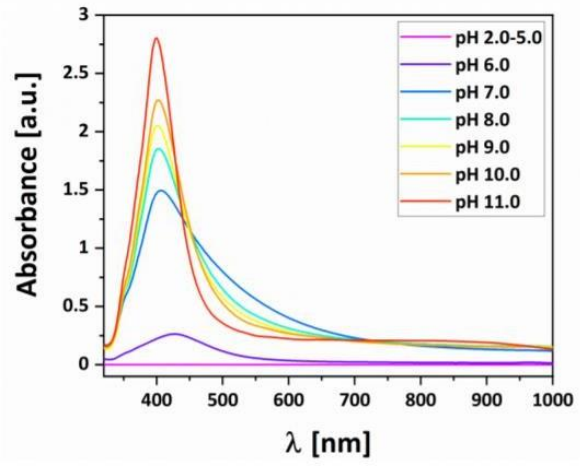

Figure 1: UV-Vis spectra of Ag nps reduced by citric acid at pH 2.0 to 11.0

Effect of temperature: As the reaction temperature increases, the rate of synthesis of the nanoparticles also increases [36]. An increase in temperature also increases the yield as seen in the increase in absorbance on increase in temperature [18]**.** An increase in the particle size with temperature is also established through kinetic studies and is probably due to a fusion growth process, **Fig 2** [37].

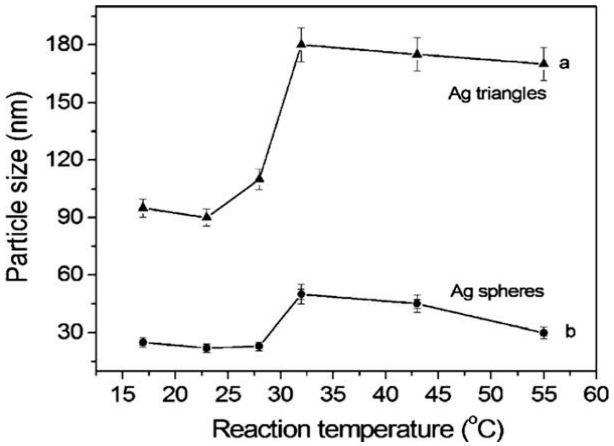

Figure 2: Average size of silver nanoplates (curve a) and nanospheres (curve b) obtained at different temperatures

Effect of concentration: As the plant extract concentration increases, the size of the silver nanoparticle decreases[38]

II. CONCLUSION

Silver nanoparticles are very useful as antimicrobial and antibacterial agents, and as antioxidants. Green synthesis of these nanoparticles is environmentally friendly, safer and less toxic. Plants provide a great source for the synthesis of silver nanoparticles. They possess a multitude of biomolecules useful for the bio-reduction of nanoparticles. However, several questions about the green synthesis of nanoparticles still remain unanswered. It is still not clearly known how nanoparticle yield differs with different biological sources, keeping the same metal salt concentration, or how the size and shape of nanoparticles alter their bio-efficacy. Is there any limitation to the use of biological sources for nanoparticle synthesis? Further research into the area is required to answer these questions.

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