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REVIEW ON THE BIOSYNTHESIS OF BIMETALLIC NANOPARTICLES USING PLANT EXTRACT AS REDUCING AND STABILIZING AGENTS

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ABSTRACT:

Bimetallic Nanoparticles grabs attention of Scientist worldwide due to fascinating properties which can be inculcate/infuse in various fields. This review provides information about Synthesis, by single pot, benign, Eco-friendly method through photochemicals. This review emphasis on influencing factors on the efficacy of extract of plant parts, the role of photochemical like phenolic acids, Flavones, Alkaloids, terpenes, carbohydrates as bio-reducing and stabilizing agents for bmnps. This review also discussed the influence of Ph of extract, Concentration of extract, Reaction time, Reaction temperature and concentration of precursor mixture on size, shape and morphology of bmnp.

KEYWORDS: *Bimetallic Nanoparticles, Phyto-Chemicals, Extract, Bio-Reducing, Stabilizing Agents.*

1. INTRODUCTION:-

Nanotechnology is the enthralling area of research, in the field of material science, medical science, life science, physical and chemical sciences (1). The prefix nano is derived from the Greek word 'nanos' meaning ''dwarf'' which refers to things of one billionth in size. Nanotechnology word was first coined by Norio Taniguchi of Tokyo University of Science. Later nanotechnology popularized by Richard Feynman; an American physicist is known as the ''Father of nanotechnology'' (2).

Particles with dimension(s) between 1 and 100 nm have been identified to be highly efficient, and of greater performance upon applications in many areas; this is because of unique strength, large surface area, catalytic property, optical activity, strong binding ability among others (physicochemical properties) displayed by the nanoparticles. These properties of nanoparticles are quite different compared to their bulk materials. (3)

This field offers us the power of manipulating the atoms or molecules and transforming them into structures having desired geometry and properties. It has both environmental and health applications which include effective drug delivery and applications in harvesting solar energy etc. It also helps in reducing the use of industrial chemicals and making the environment healthier, safer and worth living. In addition to this, it can be used for water purification, cancer treatment, as Catalyst and food packaging etc. (3).

1.1. Nanoparticles

The synthesis and properties of metallic nanoparticles (NPs) has been extensively studied over decades, not only because of their unique properties, but also because of their potential applications in catalysis, electronics, optoelectronics, information storage, biosensors, and surface-enhanced Raman spectroscopy (SERS). Nanoparticles can exist as common structural elements or composites, and they have a broad functional diversity compared to bulk materials. The physical and chemical properties of metallic nanoparticles are mostly determined by size, shape, and composition etc. parameters. (4)

1.2. Mono metallic nanoparticles

Monometallic nanoparticles (MNPs), as the name suggests, consist of only single metal. The constituted metal atom determines the properties of these nanoparticles. Monometallic nanoparticles are of different types depending upon the type of metal atom present such as magnetic, metallic and transition metal nanoparticles due to their enhanced physical and chemical properties. For this reason, they are used for several applications such as in electronic, optical (AuNPs) and catalysis (Pt, Ni), Bio-medical (AuNPs) etc. Also, they have been used as antimicrobial (AgNPs) agents against many microorganisms. (3)

1.3. Bimetallic nanoparticles

Bimetallic nanoparticles are of more interest than metal nanoparticles as they show better optical, electrical and medical applications due to their peculiar mixing patterns and synergistic effects of two metal nanoparticles that form bimetallic Nanoparticles, for example.

- BNPs have a greater surface area which increases their adsorption power and hence acts as efficient catalysts as compared to those of monometallic nanoparticles. (3) ex: Platinum-based bimetallic such as Pt-Co, Pt-Ni and Pt-Fe have very good catalytic activity. (5)
- Bimetallic nanoparticles with plasmonic(optical) properties such as Au/Ag/Cu composites are typically employed as plasmonic biosensors due to the sensitivity of their LSPR to the surrounding medium (5).
- Most imaging techniques, such as magnetic resonance imaging (MRI), computed tomography (CT), and dual-modal imaging, require the use of a contrast agent. Due to the magnetic nature of Fe, Co, or Ni bimetallic nanoparticles, these types of materials serve as good contrast agents in imaging techniques (5).
- Bimetallic can be effectively used in drug delivery as they have the high surface area to volume ratio, hence can cross the blood-brain barrier and epithelial cell junction to reach the target site. These bimetallic nanoparticles, due to their excellent electrical and optical properties can be used as biosensors (5)
- Bimetallic nanoparticles are of great importance in the restitution of the environment. Their role in decontamination of groundwater has given significant results. Fe-Cu bimetallic nanoparticles can be used in clearing nitrates in groundwater via in-situ remediation (5)
- Bimetallic nanoparticles also serve as great antimicrobials, can complement the role of antibiotics in combating with bacteria (5).
- Au-Ag BNP is used in Photothermal Cancer therapy (5).
- Since bimetallic nanoparticles are composed of two different metal atoms, the atomic distribution can greatly influence the final architectures of Bimetallic Nanoparticles. Bimetallic nanoparticles can form different architectures depending on atomic arrangements. Since there is a close relationship between structures and properties, the rational controlled synthesis of bimetallic nanoparticles is of vital importance for their applications. (6). The different architectures of BMNPs are as following types:

❖ Crown-jewel structure (5).
❖ Hallow structure (6).
❖ Hetero structure (6).
❖ Core-shell structure (6).
❖ Alloyed structure [4].
❖ Inter metallic structure [4].
❖ Sub-cluster Structure [4].

- Porous structure (6).

2) Preparation of BMNPs

There are two general approaches to synthesize the metal nanoparticles those are top-down and bottom-up.

Top-Down Approach:

The top-down approach is based on a solid-state physics strategy used to make nanostructures. This method begins with macroscopic-sized materials that are then made into structures having nanoscale sizes. The top-down approach presents challenges in producing large quantities of uniformly shaped particles; however, to circumvent these issues, a bottom-up approach can be used.

Bottom-Up Approach:

The bottom-up method requires a suitable soluble source of metal ions in the form of soluble salts or coordinated by suitable ligands. To such a solution, a reducing agent has added whose nature has a strong influence on the particle properties. The particle growth and the colloidal stability are usually controlled by suitable capping agents like surfactants, polymers, Photochemicals and polyelectrolytes.

For the synthesis of BMNPs, at least two metal ion precursors must be used, their presence during reduction determines the nature of resulting BMNP. The reduction of two Metal ion can be achieved by two modes; those are Simultaneous/Co-reduction mode and Successive/Subsequent reduction mode.

Simultaneous/Co-reduction

If both metal precursors are present at the same time, their simultaneous reduction maybe lead to alloyed nanoparticles.

Successive/Subsequent reduction

In contrast, a sequential reduction ("seeded growth") can lead to core-shell particles. For example, if A Metal ion is reduced first to A nanoparticles, the subsequent addition of B in the presence of a sufficient amount of reducing agent leads to bimetallic particles with A core and B as shell. This happens because A is nobler or having high reduction potential than B (7).

2.1. Synthesis of Nanoparticles

Much effort has been devoted to the synthesis of plasmonic metal NPs with different morphologies, and the demand for new synthetic methods is still increasing. Synthetic methods involve both physical techniques (spray pyrolysis, ball milling, sputtering, etc.) and chemical processes. The solution-based chemical methods are best suited for controlling the particle size and morphology because nucleation and growth steps can be easily monitored. This requires different hazardous chemicals such as chemical reductants and capping agents to compensate the surface energy to stabilize these NPs in the nano-size regime. However, aqueous synthesis using different natural products such as sugars, ascorbic acid, and sodium citrate has been much explored, especially for the synthesis of metallic NPs. Although these NPs are biocompatible and widely used in different biological applications, there is still demand the development of other methods that are low cost and easily scalable. In this contribution, the use of plant extracts, being renewable, easy to grow on a mass scale, and environmentally benign, have caught the attention of the researchers. These renewable bio-resources have some advantages, as they minimize the use of surfactants and allow the replacement of organic solvents by water. Plant extracts have the potential for large scale production as they are easy to handle, abundant, and inexpensive. However, less control, longer reaction times, and higher temperatures have often hindered the growth of plant extract-based biosynthetic procedures when compared to the chemical synthesis of NPs [8].

2.2. Phytochemicals assisted synthesis of bimetallic nanoparticles

Generally, the synthesis of bimetallic nanoparticles involves the mixing of two different aqueous metal solutions with a plant extract. Due to Competitive reduction in the synthesis of bimetallic nanoparticles between two metal ions with varying potentials of reduction in a solution, metal ions with greater reduction potential were reduced faster than metal ions with lower reduction potential (9).

Competitive reduction facilitates the faster reduction of metal ions. It is evident in Akinsiku, A. A. et al. (10) During the synthesis of Ag NPs, nucleation and formation of Ag nanoparticles were completed after 30mints, but in the synthesis of Ag-Ni BMNPs nucleation and formation of Ag nanoparticles completed within 5 mints in the presence of Ni ions owed to competitive reduction. Size, Shape and Morphology of synthesized BMNPs may be affected by the Reaction temperature, Reaction Time, concentrations of the extract, Concentration of precursor solution (metal ions) and pH (11).

i) Reaction Temperature

According to S.U. Ganaie et al. During the Simultaneous synthesis of Au-Ag BMNPs it is evident that as increasing temperature from room temperature to 70°c accompanied the increase in the intensity of single SPR peck which reveals that fasten the formation and nucleation of alloyed BMNP at irrespective of P^{H}. But in case of Subsequent synthesis at P^{H} =4 same trend was observed, in contrast at P^{H}=9 formation of BMNPs completed within mints at room temperature on increasing temperature had no significant impact on the intensity of SPR peak which reveals that no effect of the temperature. Alloyed and Core-Shell architecture of BMNPs were observed depending on the sequence of addition of metal ion solutions. It was noted that a high reaction temperature leads to more stable nanoparticles, but a high concentration of plant extract is required to obtain small-sized particles (9).

ii) Reaction time

Akinsiku, A. A. et al. (10) revealed that with reaction time, rate of formation of BMNPs also increases. During the synthesis of Ag-Ni BMNPs at all concentrations of precursor solutions, the intensity of single SPR peak increased with time up to 60 mints, that indicate the nucleation and growth of bnp enhanced with time. On further increment of time, the intensity of peak remains constant which means the synthesis of Ag-Ni bnps completed.

S.U. Ganaie et al. (8) observed during Sequential/Successive synthesis of Au-Ag bnps that the intensity of SPR bands at pH 4 increased gradually with time till it reached a maximum, evidently due to increasing of the concentration BNPs. At pH 10, the BNP formation was almost completed within a few minutes of the commencement of the synthesis. The intensity of the peak of the reaction mixtures increased only marginally thereafter and by the fourth hour had reached their maximum. The shape of the spectra remained unchanged, which indicates that the pattern of shape and size of bnps were unchanged. A similar trend was reported by Khalil et al. (12).

iii) P^{H} of plant extract

Khalil et al. [12] studied the efficacy of Gmelina leaf extract in the synthesis of Au and Ag nanoparticles, followed by Au-Ag bimetallic nanoparticles. In acidic medium synthesized Ag nanoparticles were unstable and precipitated within 12 hrs., while in basic medium (pH=9) are stable for one week. Increase in PH accompanied by blue shift which reveals a decrease in size associated with the change in morphology from Anisotropic to Isotropic. The same trend appeared in the case of Au nanoparticle as well as Au-Ag bmnps. A major influence of the reaction pH is its ability to change the electrical charges of biomolecules which might affect their capping and stabilizing abilities and subsequently the growth of the nanoparticles. This result was confirmed by the TEM measurement carried out at pH 5.5 and pH 9, the size and shape of Au AgNPs were affected by changing the pH of the reaction medium. The size of the AuNps was with the average size 15nm at pH 5.5 while at pH 9, smaller size in the range of 8 nm were found with different morphologies. The decrease in the size of the nanoparticles was also observed for Ag NPs and Ag-Au Nps.

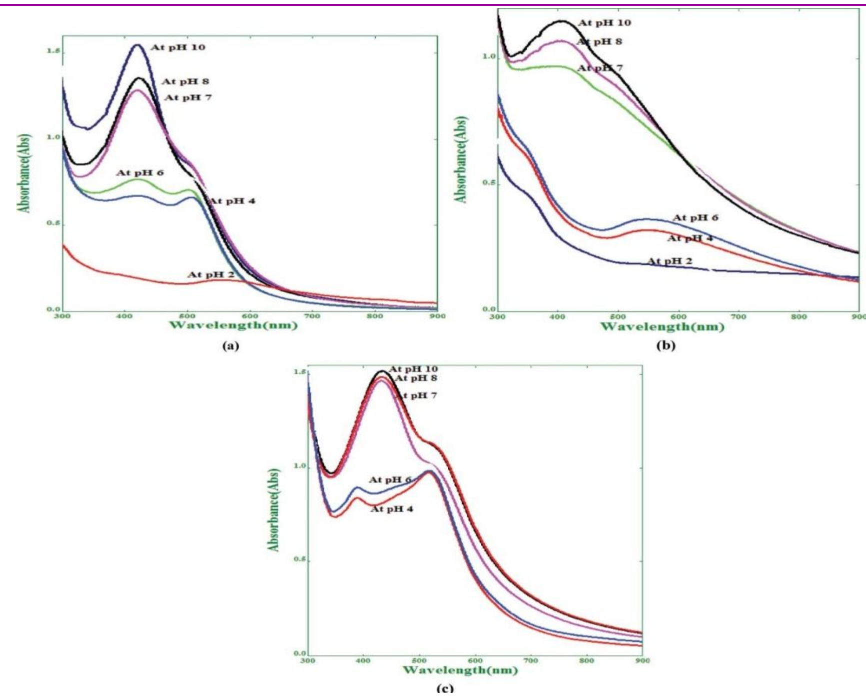

Figure 1. The UV visible absorption spectra of BNPs synthesized via (a) co-reduction of Ag(I) and Au(III), (b) addition of Ag(I) to AuNPs and (c) addition of Au(III) to AgNPs at different pH. (8).a

S.U. Ganaie et al. (8) observed the Morphology at Ph=4 to10 in Simultaneous synthesis of Au-Ag bmnps. At PH=4, at the outset of the synthesis, a single SPR peak observed around 516nm-560nm due to formation of Au nps, by proceeding the reaction another peak observed around 423nm resulted by Ag nps and assembled on the surface of Au nps to result in Core=Shell Au-Ag bmnps. In contrast, same reaction carried out at PH=10 results a single narrow SPR peak about 420-495nm due to formation of Alloy Au-Ag bmnps. If the concentration of Au(III) ion increased then peak shift towards longer wavelengths(Redshift) which implies that increase in the size of Alloyed Au-Ag bmnps.

In Subsequent reduction When Au (III) was added after the AgNP had been formed at pH 4 and 10, a single peak was seen at 450 560 nm, characteristic of Ag Au alloy NPs. A redshift in the peak was observed with the increasing proportion of Au (III) relative to Ag (I). The addition of Ag (I) to the AuNPs at pH 4 and 10 yielded a spectra characteristic of Au-Ag core-shell NPs with two peaks: at about 420 and 510 nm.

As the standard electrode potential of Au (III), Au is higher than that of Ag (I), Ag; it is possible that the replacement reaction occurring between AgNPs and Au(III) may be leading to the formation of a homogenous alloy rather than core-shell NPs.

IV) CONCENTRATION OF EXTRACT

Mostafa M.H. Khalil et al. (12) revealed that during the preparation of Au Nps with Gmelina leaf extract, the absorption spectra exhibit a gradual increase of the absorbance accompanied with a shift in the λmax from 566 to 534 nm (Blueshift). With an increase in the quantity of extract, the full width at half maximum (FWHM) decreases supporting the reduction in particle size. Further increasing the concentration of extract, the λmax was shifted to longer wavelengths (Redshift) of the AuNPs with a slight decrease in absorbance. This is most likely due to changes in the dielectric properties of the layer immediately surrounding the gold nanoparticles and to some small amount of particle aggregation.

As the concentration of the Gmelina leaf extract increases in the Ag NPs synthesis, the absorption peak gets more sharpness and the blue shift was observed from 458 to 441 nm. The blue-shifted and sharp narrow shape SPR band indicating the formation of aspherical and homogeneous distribution of silver nanoparticles was observed. In contrast to this further increased the concentration of extract resulted in a broader SPR band, suggesting an increase in particle size of Ag NPs (12).

S.U. Ganaie et al. (8) observed Concentration/proportion of extract at PH=4 @ 10. As the concentration of the extract doubled at pH 4, the spectra with two SPR bands, one at 414 and the other at 520 nm appeared. Further, the concentration of extract double favored increased formation of BNPs, which is confirmed by the greater intensity of the SPR bands. At still higher extract concentrations, the SPR bands underwent a progressive decrease in absorbance.

As the concentration of the extract was increased to 8 times at pH 10, a single SPR band at 420-495 nm region positioned between the SPR of monometallic Ag and AuNPs appeared along with the progressive increase in its intensity. A change in the shape of SPR band also occurred from broad and asymmetric to increasingly narrow and symmetric as reflected in the 'full-width at half maximum' (FWHM) values which changed from 447 to 206 nm along with a continuous shift in λmax towards lower wavelengths. This, in turn, indicates an increasing shift from polydispersion to mono dispersion with an increase in the proportion of the extract, whereas the blue the size of BNPs.

V) EFFECT OF CONCENTRATION OF PRECURSOR SOLUTION

According to Nurul Amal Nadhirah Mohamad et al. (9) changing the concentration ratio of Au to Ag ions and found that an increase in Au ions led to the formation of alloy AuAg nanoparticles. TEM imaging at a 9: 1 ionic ratio showed homogenous electron density and agreed with the single SPR band observed in UV -vis spectra. Both results supported the formation of alloy nanoparticles. At ratios of 1: 1 and 1:2, contradictory results were obtained. The high-resolution image showed electron banding suggesting the formation of core-shell nanoparticles. The claim was supported by the dual peaks observed in UV-Vis spectra corresponding to gold and silver respectively. This study also discovered that the particle size of alloy nanoparticles was slightly larger than that of core-shell nanoparticles.

Abimbola Akinsiku, A et al. (3) observed the effect of concentration of precursor solution (equimolar Concentrated) with time during the synthesis of Pseudo-Cubic Ag-Ni BMNPs via simultaneous reduction. Narrow SPR band was observed in the absorption spectra at 1.0 mM concentration, unlike broadband observed at higher concentration which could probably be as a result of anisotropic growth which led to large particle formation. The broadband also connotes aggregation of nuclei and irregular shape of Alloyed BMNPS.

Akinsiku, A. A. *et al*. (10) interpreted contrast, correlation during the synthesis of Alloyed Ag-Ni BMNPs via Simultaneous reduction at 70°C. When the concentration of extract increased from 0.5mM to 2.0mM with time, a change in the shape of SPR band also occurred from broad and asymmetric to increasingly narrow and symmetric without any shift in wavelength(421nm), which suggests that presence of spherically shaped and smaller Alloyed Ag-Ni nanoparticles. In contrast, when concentration of extract is changed to 3.0mM then broad peak and Redshift observed, suggested aggregation and polydispersed structures.

3. CONCLUSION

This review suggests the facile, single step. Benign synthesis of Bimetallic Nanoparticles may promote green chemistry. This review emphasis on green protocols for reduction and stabilization of metal nanoparticles. Plant extracts contain secondary metabolites (such as phenolic acid, Flavonoids, Alkaloids, Carbohydrates etc.) acted as both reducing and stabilizing agents in the production of bimetallic nanoparticles. Utilization of plant extract has eliminated the requirement for Sophisticated equipment , extreme conditions (like hing temperature, energy and pressure), high energy, hazardous chemical as reductants and stabilizing agents during in this process, and also discussed about the influencing factors on Nanoparticles sizes, shape and morphology which can be can be controlled by varying the pH, reaction temperature ,concentration of plant extract and as well as the Concentration of precursor solution.

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