

Synthesis of Silver Nanomaterials Capping by Fruit-mediated Extracts and Antimicrobial Activity: A Critical Review

ABSTRACT

Natural silver nanoparticles are currently being used innovatively by a unique simple route. Different bio-mediated fruit peel extracts were used to produce silver nanoparticles (AgNPs) and explore the synthesis of environmentally friendly aspects. To produce biodegradable AgNPs various bio-mediated fruit peel extracts function as reducing and capping agents in the synthesis route. It was discovered that several fruit peel extracts act as a capping agent and silver ions (Ag^+ to Ag^0). Due to reduction, the reaction changes the hydrogel's distinctive hue to a reddish-brown appearance. UV-visible spectra of the AgNPs showed a distinctive surface plasmon resonance (SPR) peak around 460.0 nm. Using X-ray diffraction, the crystallographic nature was discovered with Bragg's diffraction. FT-IR confirmed silver ions function as a capping and reducing agent from peel extract. The transmission electron microscope confirmed that the average size of the nanoparticles was below 100.0 nm and internal morphology. These nanoparticles' ability to combat bacteria, algae and fungi was also well investigated. This manuscript highlights the different bio-mediated and peel extracts that are efficient in producing AgNPs and their function for promising antimicrobial activity.

Keywords: Bio-mediated, nanoparticles (NPs), peel extracts, reducing agent, silver nanoparticles (AgNPs).

1. Introduction

The function of nanotechnology in science and technology is to create novel, unique and unified materials at the nanoscale [1]. One billionth of a meter like 10^{-9} is denoted by the term nano. In

1974, Tokyo Science University professor Norio Taniguchi first used nanotechnology to refer to the precise synthesis of materials at the nanoscale level [2]. Nanoparticles have distinct chemical, optical and mechanical capabilities, their application is becoming more popular in the twenty-first century [3]. Although the formation of AgNPs by chemical and physical means has been thoroughly investigated, one crucial area of nanotechnology is developing dependable natural technology to produce nanoparticles [4]. Enzymes and bacteria are proposed as potential natural substitutes [5]. Because noble metal nanoparticles like silver have special optical, electrical, mechanical, magnetic, size-dependent and chemical properties. There has been an increase in the focus of current studies on these nanoparticles and the bulk materials differ greatly from one another [6]. Metal nanoparticles have important uses in electronics, optoelectronics, magnetic, biological and information storage systems because of these size-dependent characteristics [3, 6]. Metal nanoparticles can be synthesized using a variety of methods, including chemical, electrochemical, photochemical and radiation. Toxic compounds produced by the chemical technique may negatively affect human health and medical applications [6]. The biosynthesis of nanoparticles is required to serve as the primary driving force underlying the widely recognized bottom-up technique known as metal nanoparticle biogenesis [6]. When compared to chemical approaches, this method produces safer more affordable and ecologically friendly nanoparticles [7]. It is more convenient to use agricultural waste such as bio-mediated peel extracts to produce nanoparticles than it is to use other benign biological processes. Fruit peels are particularly readily available, effective, reasonably priced, natural, eco-friendly and abundant in bioactive components [7]. Since these bioactive substances have potential applications as antibacterial and antioxidants. Most researchers are working to find a productive method of removing these substances from fruit peels [7]. There are numerous methods for creating silver nanoparticles. For example, facile method [8], thermal decomposition of silver compounds [9], electrochemical [10], Sono chemical [11], microwave-assisted process [12] and recently via green chemistry

route[13]. To create ecologically safe methods for synthesizing AgNPs without the use of hazardous compounds is expanding [8, 13]. The use of microorganisms or plant extracts in biosynthetic processes has made them a straightforward and practical substitute for physical and chemical synthetic processes. Compared to other biological processes, the extract that serves as a reducing and capping agent for the production of nanoparticles has greater advantages [8, 14].

The plant's nanoparticles are favoured because they are affordable, environmentally beneficial, a one-step procedure for biosynthesis and safe for humans [10-13]. Various substances including extracts [11], fruit [12], bark [13], fruit peels [14], root [15] and callus [16] have been investigated thus far for the production of silver nanoparticles in different sizes, shapes and forms. Plant extracts are used to synthesize natural nanoparticles. All across the world, people eat bananas, papaya, dragon fruits etc. and after the pulp is eaten the peels are usually thrown away [18]. Among the uses for banana peels that have been covered in the literature are used for their therapeutic qualities [19], production of ethanol [20], foundation for the production of fungal biomass [21], synthesis of laccase [22] and biosorbent to remove heavy metals [23]. Furthermore, banana peels which are naturally abundant in polymers like cellulose, hemicellulose, lignin and pectin might be applied to the production of AgNPs[23]. Catalytic activity and other associated qualities such antibacterial activity of AgNPs are correlated with specific surface area. Because surface energy rises with increasing specific surface area, nanoparticles may potentially become more biologically useful [23, 67]. In medicinal and pharmaceutical uses, noble metal nanoparticles come into direct contact with the human body, like toothpaste, shampoos, soaps, detergents, shoes and cosmetics [24]. Given the increasing microbial resistance to metal ions, antibiotics and the emergence of resistant strains, researchers are becoming increasingly interested in metallic nanoparticles which exhibit promising antibacterial properties due to their large surface area to volume ratio [7, 24]. With the use of an

extract made from leftover banana peels, phytochemicals [24, 69] etc. seek to create silver nanoparticles in an environmentally friendly manner. The AgNPs were characterized using a variety of techniques SEM, TEM, XRD and FTIR [50-55]. AgNPs are **inorganic antibacterial agents** that are harmless and nontoxic and they can eradicate approximately 650.0 different types of microbes that cause diseases [25-26]. From this point of view, we overview the studies that are easy to find even being envisioned as antibacterial agents of the future any potential aspect.

2.0. Materials and Methods

2.1. Materials

A different variety of fruit peels were screened from the nearby area. After being retrieved from the nearby place such as pomegranate, banana, papaya and dragon fruits in Fig. 1. The peels were taken off and allowed to air dry and investigated crucially. The different parts of these peels were investigated and the best-fitted data was found to be investigated scientifically.

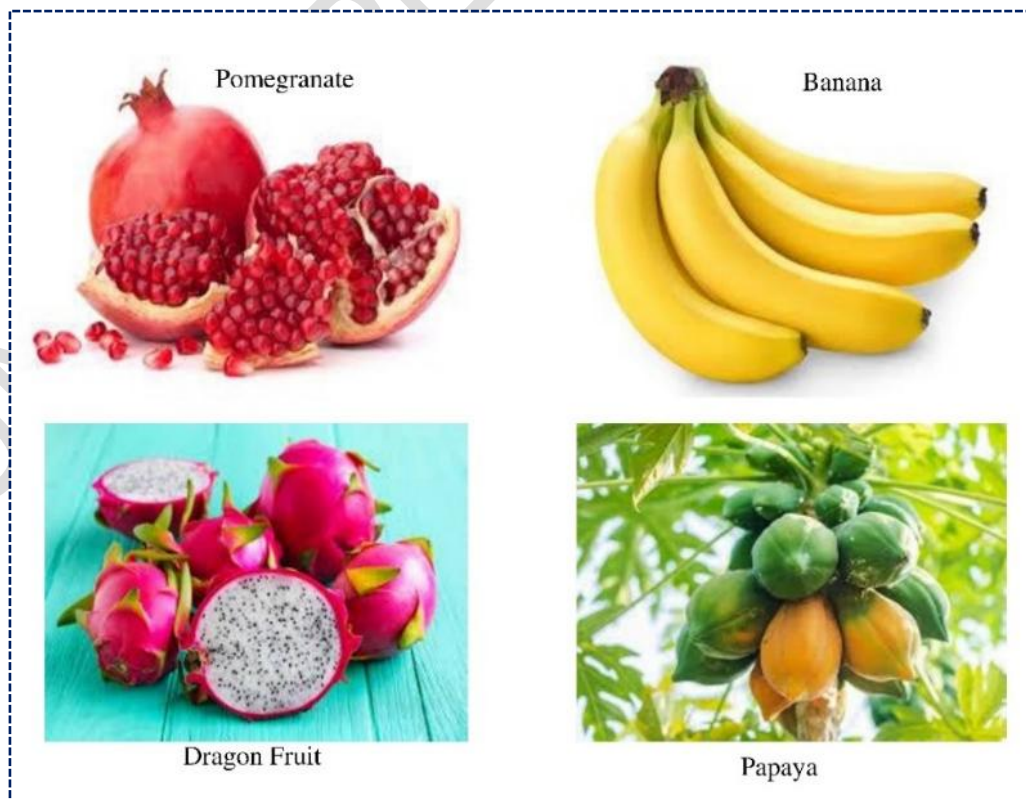


Fig. 1. Source of different bio-mediated peel extracts.

2.2. Methods

AgNPs are synthesized by the main three possible routes physical methods, chemical methods and biological methods. The three routes follow the possible approach such as the top-down approach and the bottom-up approach [27]. The atoms are submerged in the bottom-up approach and in another way, the bulks are decomposed into smaller ones in a top-down approach [27] expressed in Table 1.

Table 1. Synthesis procedure of nanomaterials

| Methods | Description | Type | Nature |
|--------------------|---|--------------------|----------|
| Physical methods | Laser ablation, high energy ball-milling, electro-spraying, inert gas condensation, physical vapour deposition and laser pyrolysis etc. | Top-down approach | Toxic |
| Chemical methods | Sol-gel method, microemulsion techniques, hydrothermal analysis, polyol synthesis, chemical vapour synthesis etc. | Bottom-up approach | Toxic |
| Biological methods | Steam, roots, leaves, latex, buds, flowers, seeds, bacteria, fungi, yeast, microalgae, macroalgae etc. | Bottom-up approach | Nontoxic |

The bio-mediated peels were cut into little pieces and peels were then cleaned three times using tap water and distilled water to get rid of any external dirt impurities [28]. On paper towels, the peels were then taken off and allowed to dry. After adding 50.0 ml of double-distilled water to a 100.00 ml beaker with about 25.0 g of peel, the mixture was brought to a boil at 800.0 °C for 10.0 minutes [28]. The peel was then filtered twice using Whatman filter paper to exclude macromolecules. As a self-reducing agent in this, banana and papaya peel extract work. To reduce silver nitrate into AgNPs, around 5.0 ml of filtered bio-peel extract is collected, added to 1.0 mM of pure aqueous silver nitrate solution and agitated for 1.0 hour [28]. The solution changes colour from yellow to brownish yellow to deep brown as a result of the reduction process of Ag^+ to Ag^0 and confirmed the formation of nanoparticles. The creation of a brown colour indicates that the AgNPs synthesis was finished [28].

Table 2. Bacterial-mediated synthesis of AgNPs

| Bacteria | Silver salt | Shape | Size | Application | References |
|------------------------------------|-------------------|-----------|-----------|---|------------|
| <i>Lactobacillus acidophilus</i> | AgNO ₃ | Spherical | 10.0-20.0 | Antioxidant and antimicrobial activity | [29] |
| <i>Bacillus cereus</i> | AgNO ₃ | Spherical | 20.0-40.0 | Antioxidant and Antibacterial activity | [30] |
| <i>Bacillus sp.</i> | AgNO ₃ | Spherical | 22.0-41.0 | Antifungal activity | [31] |
| <i>Pseudoduganel la eburnean</i> | AgNO ₃ | Spherical | 8.0-24.0 | Antimicrobial activity | [32] |
| <i>Bacillus siamensis</i> | AgNO ₃ | Spherical | 25.0-50.0 | Antibacterial activity | [33] |
| <i>Phenerochaete chrysosporium</i> | AgNO ₃ | Spherical | 34.0-90.0 | Antibacterial activity | [34] |
| <i>Bacillus brevis</i> | AgNO ₃ | Spherical | 41.0-68.0 | Antibacterial activity | [35] |
| <i>Streptomyces sp.</i> | AgNO ₃ | Spherical | 10.0-30.0 | Antibacterial activity and antiviral activity | [36] |

A comparable procedure is used to produce AgNPs using different amounts of papaya and banana peel extract from carioca [28] as well as different sources of bacteria, fungus and algae mediated also applied for the synthesized of silver nanomaterials illustrated in Table 2 to Table 4.

Table 3. Fungal medical synthesis of AgNPs

| Fungus | Silver salt | Shape | Size | Application | Reference |
|-------------------------------------|-------------------|-----------|------------|-----------------------|-----------|
| <i>Talaromyces purpureogenus</i> | AgNO ₃ | Spherical | 50.0-70.0 | Antifungal | [37] |
| <i>Trichoderma harzianum</i> | AgNO ₃ | Spherical | 31.13 | Antifungal | [38] |
| <i>Anamorphus bjerkantera</i> | AgNO ₃ | Spherical | 70.0-90.0 | - | [39] |
| <i>Penicillium verrucosum</i> | AgNO ₃ | Spherical | 10.0-12.0 | Antifungal | [40] |
| <i>Aspergillus brunneoviolaceus</i> | AgNO ₃ | Spherical | 0.72-15.21 | Antioxidative acidity | [41] |
| <i>Penicillium oxalicum</i> | AgNO ₃ | Spherical | 60.0-80.0 | Antifungal | [42] |
| <i>Setosphaeria rostrata</i> | AgNO ₃ | Spherical | 2.0-20.0 | Antifungal | [43] |
| <i>Fusarium scirpi</i> | AgNO ₃ | Spherical | 2.0-20.0 | Antifungal | [44] |

Table 4. Algal-mediated synthesis of AgNPs

| Algae | Silver salt | Shape | Size (nm) | Application | Reference |
|------------------------|-------------------|-----------------------|-----------|--|-----------|
| Chaetomorpha Ligustica | AgNO ₃ | Spherical | 2.0-12.0 | Anticancer | [45] |
| Chlorela vulgaris | AgNO ₃ | Spherical | 55.0 | Photocatalytic dye degradation acidity | [46] |
| Gelidium Corneum | AgNO ₃ | Spherical | 20.0-50.0 | - | [47] |
| Noctiluca Scintillans | AgNO ₃ | Spherical | 4.50 | Antibacterial | [48] |
| Botryococcus braunii | AgNO ₃ | Cubical and spherical | 40.0-90.0 | Antimicrobial | [49] |

3.0. Characterization Technique

Different type of techniques was employed for the characterization of AgNPs such as spectroscopic, X-ray and microscopic listed in Table 5. The spectroscopic techniques interact with the nanomaterials which produce different signals that can calculate the optical properties, synthesis and stability of NPs by UV-visible; investigate the phytochemical's role in NPs synthesis by FTIR and determine the hydrodynamic diameter and polydispersity index of NPs by DLS [50-52]. Determine the crystalline size, shape, structure, lattice parameters, stress, strain, dislocation density, lattice volume and particle size of NPs, surface morphology, shape, size and electrical and mechanical properties of NPs by X-ray [53].

Table 5. Common techniques for the characterization of silver nanoparticles

| Techniques | Characterization techniques | Information provided | References |
|--------------------------|-----------------------------|---|------------|
| Spectroscopic techniques | UV-visible | Optical properties, synthesis and stability. | [50] |
| | FTIR | phytochemical's role. | [51] |
| | DLS | hydrodynamic diameter and polydispersity index. | [52] |
| X-ray based techniques | XRD, XAS, XRF, XPS | crystalline structure and particle size. | [53] |
| | AFM | Surface morphology, shape, size, electrical, and mechanical properties. | [53] |

| | | | |
|-------------|-----|---|------|
| Microscopic | SEM | Particle size distribution, morphology and topography. | [54] |
| | TEM | Morphology, shape, size, elemental composition and electrical conductivity. | [55] |

The internal and surface morphology, shape, size, elemental composition, impurities, lattice freeze and electrical conductivity of NPs by scanning electron microscope and transmission electron microscope [55].

4.0. Results and Discussion

4.1. Visible observation

Fig. 2. shows that the mixture of artificially created AgNPs is made with papaya peel extracts in different concentrations as 5.0 ml, 10.0 ml, 15.0 ml, 20.0 ml and 25.0 ml [56]. Fig. 2. which shows the colour variation of the reaction mixture 1.0 hours after the reaction started, shows how the concentration of *Carica papaya* bio-mediated peel extracts utilized has **an affected** [56]. With an increase in peel extract concentration from 5.0 ml to 25.0 ml, the reaction mixture's colour from reddish brown to brown increases and conformation nanoparticles are formed [56].

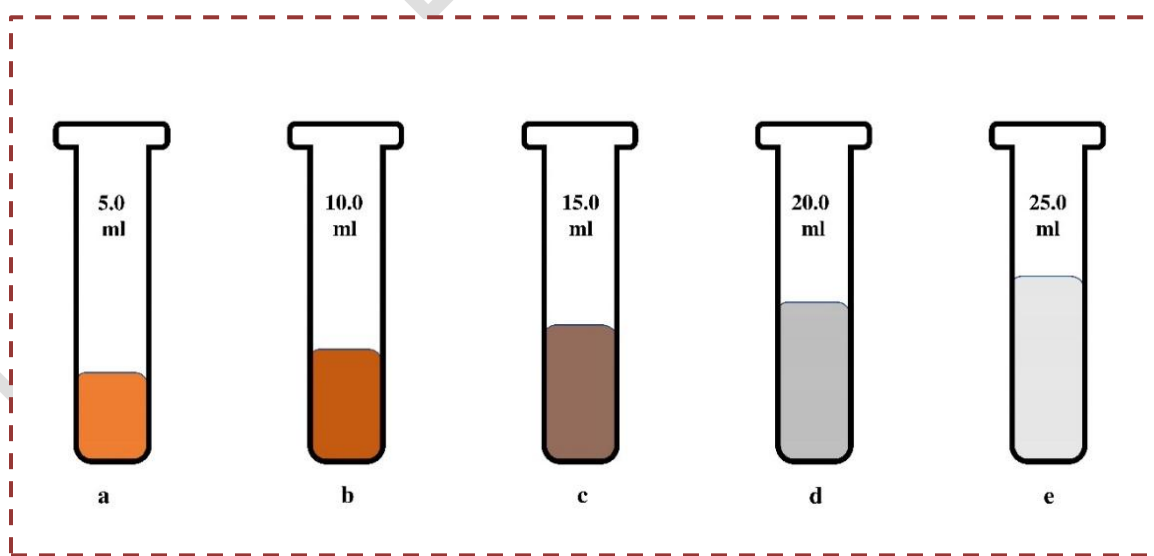


Fig. 2. AgNPs using (a) 5.0 ml, (b) 10.0 ml, (c) 15.0 ml, (d) 20.0 ml, (e) 25.0 ml of *Carica papaya* peel extract after 1.0 h of incubation.

4.2. UV-visible Spectra Analysis

After the 24.0-hour incubation period, the UV visible absorption spectra of AgNPs at five distinct concentrations 5.0 ml, 10.0 ml, 15.0 ml, 20.0 ml and 25.0 ml of the aqueous papaya peel extract at room temperature peaks are found at 410.0 nm, 420.0 nm, 435.0 nm, 422.0 nm and 418.0 nm respectively [57]. The absorption SPR band is detected for 5.0 ml, 10.0 ml, 15.0 ml, 20.0 ml and 25.0 ml concentrations of papaya peel-mediated silver nanoparticles [57]. At 15.0 ml and 25.0 ml concentrations, the SPR peak with maximum and minimum intensity is detected at 435.0 nm and 418.0 nm [57].

Table 6. The optical band gap of papaya peel extracts from *Carica*

| Sample | Optical Band Gap (eV) | Reference |
|---------|-----------------------|-----------|
| 05.0 ml | 4.9 | [56-58] |
| 10.0 ml | 4.7 | [56-58] |
| 15.0 ml | 4.6 | [56-58] |
| 20.0 ml | 4.7 | [56-58] |
| 25.0 ml | 4.8 | [56-58] |
| 10.0 ml | 2.5 | [79] |
| 10.0 ml | 3.4 | [80] |

The papaya peel extract concentration rises from 5.0 to 15.0 ml and the optical band gap reduces, confirming that the energy band gap also lowers as particle size increases [58]. The optical band gap is found to rise as the papaya peel extract concentration is increased to 20.0 ml and 25.0 ml, confirming the decrease in the size of the AgNPs for these concentrations which may also be supported by further XRD analysis [58, 79].

4.3. FT-IR Analysis

Bio-mediated carica papaya peel extract's FT-IR transmission spectra absorption bands near 2924.09 cm^{-1} , 2862.36 cm^{-1} and 1458.18 cm^{-1} , 979.84 cm^{-1} can be indicative of C-H alkene stretching or bending vibrations [58]. The bands located approximately at 3726.47 cm^{-1} and

918.12 cm^{-1} respectively are ascribed to carboxylic acid vibrations that are either stretching [58]. The bands located approximately at 1188.15 cm^{-1} and 1658.78 cm^{-1} can be attributed to amide I and II N–H bending which result from protein peptide bonds and carbonyl stretching, respectively [59]. When compared to pure carica papaya peel extract, the bands around 3100–3400 cm^{-1} and 1600–1650 cm^{-1} respectively due to carboxylic and amine groups are shifted to higher wavelengths due to the binding of silver ions and the depth of the band decreases [60].

4.4. X-ray Diffraction (XRD) Analysis

The XRD patterns unequivocally demonstrate the crystallographic nature of the AgNPs produced by the bio-reduction of silver ions in papaya peel broth. The phase distribution, crystallinity, dislocation density, lattice parameters and purity of the produced AgNPs are assessed by XRD [81]. The two thetas (2θ) values in the diffractogram of the AgNPs range from 20.0° to 90.0° [81]. There are five unique diffractions for the cubic crystal of AgNPs which are (111), (200), (220), (311) and (222) predominant plane when indexed under the standard [61][JCPDS] Card [No. 04-783] in Fig. 3. [81].

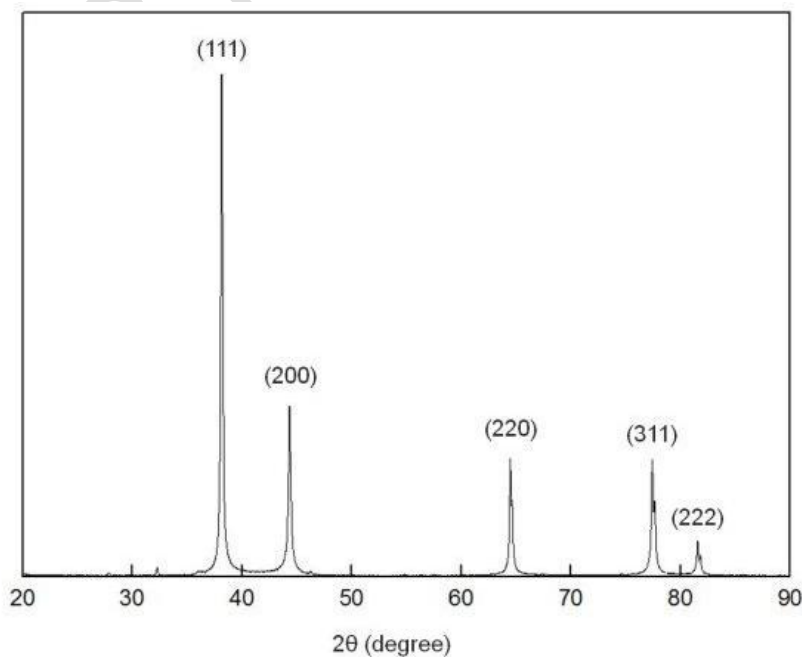


Fig. 3. X-ray diffractogram of AgNPs

Peel extract may account for the diffraction seen at 27.0° and 32.0°. A capping chemical stabilizing the nanoparticles may have caused these Bragg's diffraction [62]. The crystallite sizes of the AgNPs at different concentrations of papaya peel extract are determined [63] by the Debye-Scherrer model denoted equation 1.

$$D = \frac{K\lambda}{\beta \cos \theta} \text{-----(1)}$$

The average crystallite size was determined to be 16.1 nm, 16.3 nm, 17.9 nm, 17.8 nm and 17.7 nm respectively for papaya peel extracts varying concentration [63]. The average crystallite size of the particles is found to grow when the papaya peel extract concentration rises. The average crystallite size of the particles then gradually declines as the concentration rises to a low volume [64]. The percentage of crystallinity and lattice parameters [82-90] also investigated the NPs. The UV visible spectrum examination could verify the particle's decreased crystallite size. Further observations reveal that the synthesized AgNPs have a crystallite size that is significantly less than the 28.0 nm reported [64]. This reduction in crystallite size improves the AgNPs characteristics [68].

4.5. SEM Analysis

SEM analysis is performed to study the surface morphology and shapes of AgNPs illustrated in Fig. 4.[78]. For *Carica papaya* peel is observed that the AgNPs are spherical and the concentration of the extract alters the size and shape of the NPs[58].

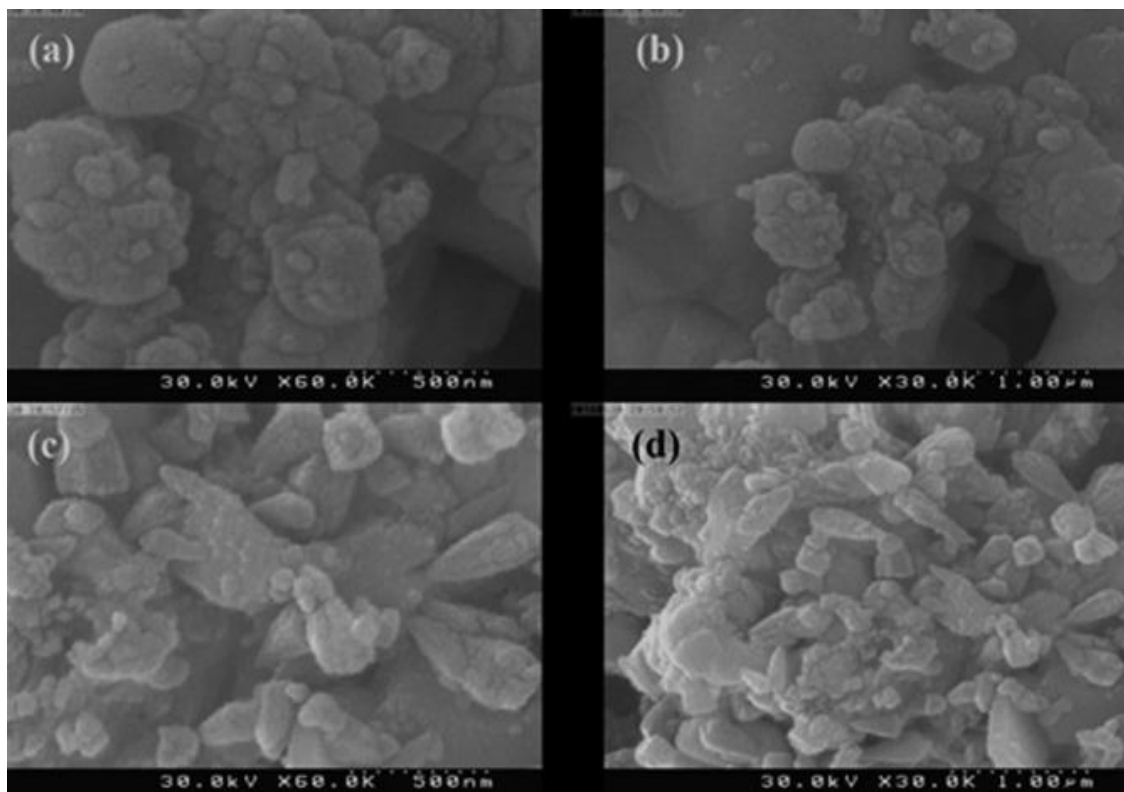


Fig. 4. SEM images of silver nanoparticles using pomegranate peel extract

The particles are uniformly distributed and no aggregations are observed at low concentrations. However, the particles get agglomerated as the concentration of papaya extract and pomegranate peel extract increases for high concentrations [58, 78]. The agglomeration of particles leads to the destabilization of AgNPs [58, 78].

4.6. TEM analysis

TEM images of AgNPs synthesized using peel are shown in Fig. 5 [58]. AgNPs size and form in the solution change with extract concentration. Mostly spherical NPs shape is suggested by these image profiles [58]. There are also a few isolated NPs in some areas, suggesting that sedimentation may have occurred later [66].

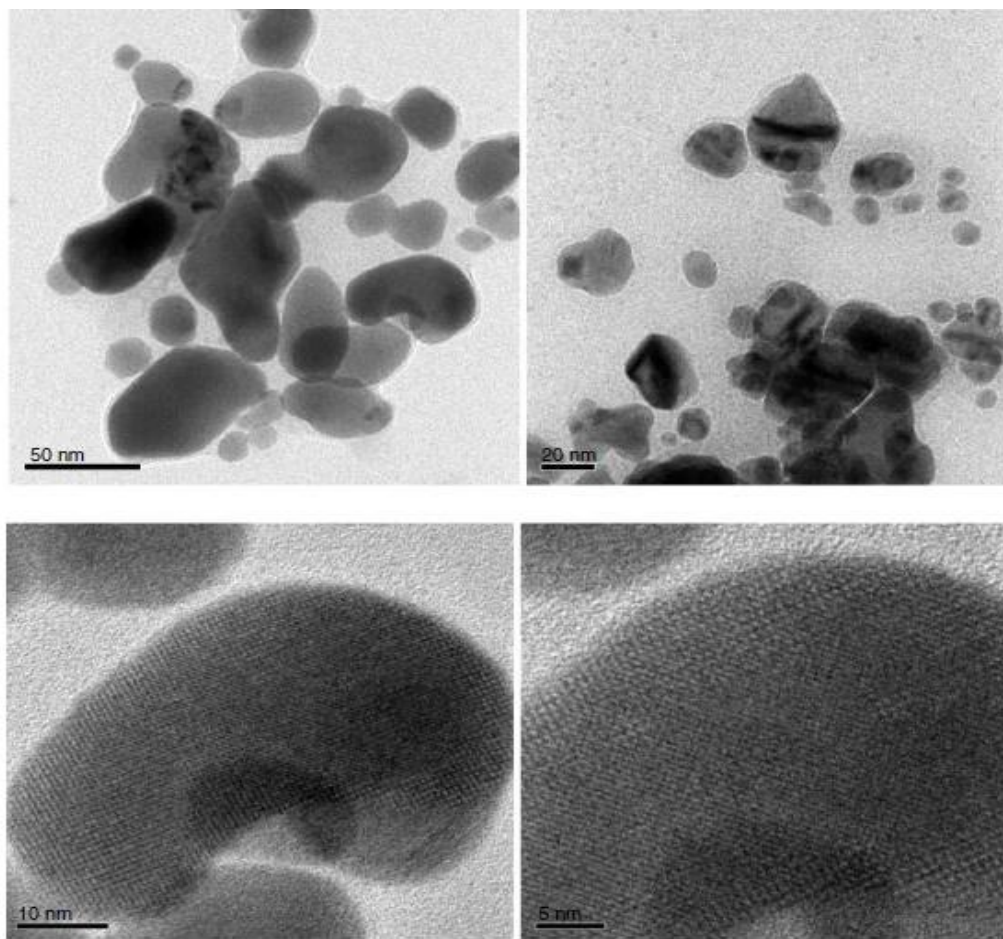


Fig. 5. TEM images of AgNPs using peel extract

The range of 15.0 nm to 20.0 nm is reported to be the average particle size of AgNPs. Parallely proved with the crystallite size determined by XRD analysis as well as TEM the results show good agreement for argument [66].

5.0. Antimicrobial Activity of Silver Nanoparticles

The bio-mediated plant parts such as the leaf, root etc into silver species show outstanding antimicrobial, anticancer, antifungal, cytotoxicity as well as catalytic activity and numerous applications [70-75, 91]. The properties also depend on its substrate, shape and size impact this antimicrobial activity as well as the surface-to-volume ratio that is responsible for demineralization listed in Table 7 [76].

Table 7. Antimicrobial activity of silver nanoparticles

| Plants | Plant's part | Shape | Substrates | Applications | References |
|---|--------------|-----------|-------------------|-----------------------------|------------|
| Allium fistulosum, TabernaemontanaDivaricata and Basella alba | Leaf | Rod | AgNO ₃ | Antimicrobial | [70] |
| Tridax procumbens | Leaf | Spherical | AgNO ₃ | Antimicrobial, anticancer | [71] |
| Aloysia citrodora | Leaf | Spherical | AgNO ₃ | Antifungal | [72] |
| Alhagi graecorum | Leaf | Spherical | AgNO ₃ | Cytotoxicity and antifungal | [73] |
| Rubus ellipticus | Root | Spherical | AgNO ₃ | Antibacterial | [74] |
| Rhodiola imbricata with aniasomnifera | Root | Spherical | AgNO ₃ | Catalytic activity | [75] |

For example, the plant Allium Fistulosum, TabernaemontanaDivaricata and Basella Alba leaf extract produced AgNPs that are rod shape effective for antimicrobial activities [70].

In the agar diffusion test, there was no growth inhibition zone around in disks with 1.00 % and 2.00 % concentrations. However, in Fig. 6. a growth inhibition zone was seen in 5.00 % concentration, with a diameter of 9.50 ± 0.70 mm for *S. mutans*, 8.50 ± 0.70 mm for *S. sanguis* and 8.00 ± 1.40 for *L. acidophilus* [77]. So, the AgNPs show outstanding microbial properties.

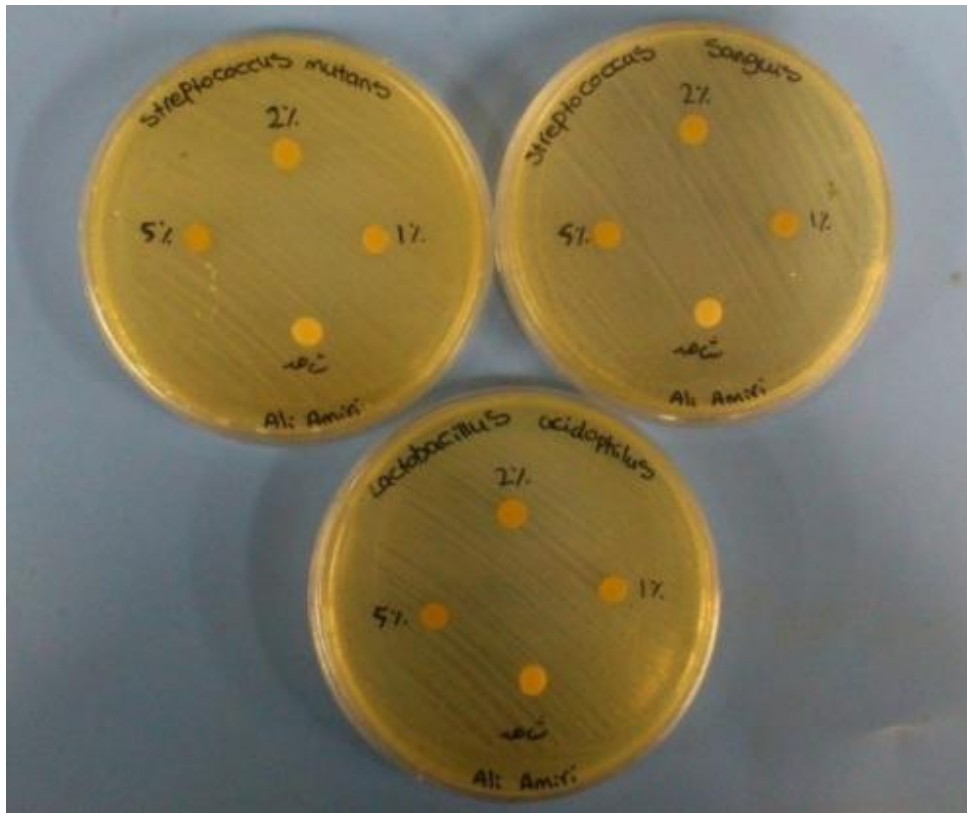


Fig. 6. Growth inhibition zone of microbes

Conclusion

Different doses of bio-mediated peel extract as the reducing agent and capping agent are discussed for the effective green production of AgNPs. These NPs are entirely safe and kind to the environment. The absorption peaks in the UV visible spectra of AgNPs for varying doses are explained. When the peel extract concentration is low then the optical band gap decreases and the absorption peaks redshift, indicating an increase in particle size. Furthermore, it is seen that the absorption peaks blue shift and the optical band gap widens as the concentration of peel extract is high. These observations suggest that the particle size will decrease. By XRD these differences in particle size may also be verified. By displaying the relevant bands that are in charge of converting silver ions into AgNPs, the FTIR spectra verify the existence of different functional groups. The average crystallite diameters of the crystalline AgNPs as revealed by the X-ray diffractograms are found to be between 16.0 and 18.0 nm which is in good agreement with

the results of the TEM investigation. Different microbes were investigated for the antibacterial efficacy of AgNPs. It was discovered that bacteria, algae and fungi have a larger zone of inhibition. This might be because there are more AgNPs in the reaction mixture.

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Conflict of Interest

The authors declare that no financial or personal relationship could influence this research manuscript.

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