



Green Synthesis of Silver Nanoparticles Using Various Food Wastes

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Abstract

Silver nanoparticles (AgNPs) can be utilized in a wide variety and very interesting applications, so they are in increasing demand. The aim of the present study was to use eco-friendly, rapid, and simple method for green synthesis of AgNPs using natural, low cost, and non-toxic reducing agents, which are alternative to hazardous chemical reducing agents utilized in traditional chemical methods. The present study reports the production of AgNPs using five aqueous extracts of pomegranate peel, banana peel, orange peel, tangerine peel and lemon peel as reducing agents and 0.01 M silver nitrate solution as chemical precursor. Each extract was added to AgNO₃ solution separately in 1:1 proportion. AgNPs were characterized by ultraviolet-visible (UV-Vis) spectroscopy, Particle Size Analyzer (PSA), X-Ray diffraction (XRD) and Fourier transform infrared (FTIR). The synthesis of AgNPs was confirmed by the change of color of AgNO₃ from colorless to dark brown color. UV-Vis Spectrophotometer showed a characteristic absorption peak around 470 nm that corresponding to the plasmon resonance of AgNPs. PSA showed that the mean of particle size of AgNPs produced using pomegranate, banana, orange, tangerine and lemon peel extracts were 9.5, 16.2, 391.3, 68.3, and 25.1 nm respectively. The XRD analysis showed that the AgNPs are crystalline in nature and have face-centered cubic geometry. This method can be used as economic, single- step, clean and green chemistry- based route for large-scale production of stable AgNPs. This approach supports the dual purpose of agricultural food waste management.

Keywords: Eco-Friendly; Silver nanoparticles; Food wastes; Green synthesis.

1. Introduction

Nanotechnology is a versatile subject, which deals with biology, chemistry, physics and engineering. Nanoparticles are clusters of atoms in the size of 1-100 nm. They are the building blocks of nanotechnology applications [1]. Nanotechnology involves the synthesis of nanoparticles that exhibit different sizes, shapes and morphology. Metal nanoparticles exhibit unique chemical, physical and biological multifunctional properties compared to their bulk parent materials so they can be utilized in a wide variety of novel applications in various fields [2]. Nanotechnology is swiftly gaining renovation in a large number of fields such as health and health care, cosmetics, biomedical, food and feed, drug-gene delivery, environment, mechanics, optics, chemical industries, electronics, space industries, energy science, catalysis, light emitters, single electron transistors, nonlinear optical devices and photo-electrochemical applications [3]. AgNPs have multi-field applications such as food industry [1], environment [4], biomedical [5], health care [6], textile, catalysis, chemical industries, space industries, energy science, optics, and microelectronics [6]. Several methods have been used to form nanoparticles. One of the simplest ways to form nanoparticles is the chemical reduction reaction in aqueous conditions. It is a chemical reaction that occurs between two components. One of them is the nanoparticles precursor, while the other acts as reducing agent. Several researchers change the chemical reagent with natural products that are enriched with reducing agents [7]. Many plant metabolites could be involved in bio-reduction, formation and stabilization of metal nanoparticles such as proteins, amino acids, polysaccharides, alkaloids, terpenoids, tannins, flavonoids, phytosterols, phenols and vitamins [8]. Recycling of

natural product waste is one of the most important innovative approaches to minimize or eliminate the use and/or generation of hazardous substances [1]. The route of synthesis of nanoparticles controls their shape and size. Nanoparticles have shape and size-dependent properties, so there are increasing demand not only to researches related to applications of nanoparticles but also to researches related to the approaches of the synthesis of nanoparticles [9]. More emphasis should be accorded to employing plant waste for nanoparticle synthesis, considering that it serves the dual purpose of waste management [2]. Production of nanoparticles by conventional chemical and physical methods may have considerable drawbacks such as defective surface formation, low production rate, high cost, large energy requirement, environmental defect, usage of toxic chemicals and formation of hazardous by-products that may have undesirable effects in pharmaceutical and biomedical applications [2, 10]. Hence, the aim of this study is to develop clean, non-toxic, eco-friendly, and safe procedures for the production of nanoparticles.

2. Materials and Methods

2.1 Chemicals and Materials

Silver nitrate was purchased from Sigma-Aldrich Chemicals. Five fruits (pomegranate, banana, orange, tangerine and lemon) were purchased from local market (Alexandria, Egypt).

2.2 Preparation of Plant Extracts

The Five fresh peels of pomegranate, banana, orange, tangerine and lemon (fig. 1) were washed repeatedly with distilled water to remove the dust and organic impurities, and then dried on paper towelling. Peels were cut into small pieces. About 5g of peels were heated with 200 mL distilled water separately at 30 – 40 °C for 20 min., cooled and filtered using Whatman No. 1 filter paper. The resultant filtrates were collected and stored at 4° C for further experiments [11].

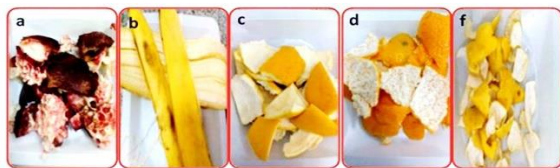


Figure 1. A digital imaging of Fruits peels used for synthesis of silver nanoparticles. a, pomegranate peel; b, banana peel; c, orange peel; d, tangerine peel; e, lemon peel.

2.3 Green Synthesis of Silver Nanoparticles Using Plant Extract

Prepared plant extract (5 mL) was added to 5 mL of 0.01 M silver nitrate solution at a temperature of about 50-60 °C till color of the mixture change [11]. Reduction of silver ions into silver nanoparticles commonly followed by colour change and the

formation of AgNPs can be visually observed [12].

Therefore, the change of colour was visually monitored to check for the formation of AgNPs.

2.4 Characterization of Synthesized Silver Nanoparticles

2.4.1 Visual Observation of the Synthesized Nanoparticles

Change in color was visually observed in the five reaction mixtures. The primary detection of silver nanoparticles was observed by visual colour change.

2.4.2 UV-Vis Spectroscopy Analysis

UV-Vis refers to absorption spectroscopy in the UV-Vis spectral region. This means it uses light in the visible and adjacent near-UV and near-infrared ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions [13]. The reduction of silver ions was monitored by measuring the UV-Vis spectra of the solutions. UV-Vis spectral analysis was performed through a UV-Vis spectrophotometer (Shimadzu, UV-1700, Japan) with resolution of 1 nm and at the range of 300-600 nm. The double-distilled deionized water was used as blank.

2.4.3 Particle Size Analyzer

The average of particle size of AgNPs was determined using a particle size analyzer (90 Plus Particle Size Analyzer, Brookhaven Instruments Corporation).

2.4.4 X-Ray Diffraction analysis

Reaction mixtures were lyophilized with lyophilizer (MartinChrist, Germany) and the dried mixtures were analyzed for the crystalline nature using an X-ray diffractometer (Shimadzu, XRD-6000, Japan) equipped with Cu K α radiation source using Ni as filter at a setting of 30 kV/30 mA. All XRD data were collected under the experimental conditions in the angular range $3^\circ \leq 2\theta \leq 50^\circ$.

2.4.5 FTIR

FTIR spectra of metal nanoparticles were recorded by using FTIR spectrophotometer (Model RXI, Make Perkin Elemer) in the range of 4000 - 400 cm^{-1} using KBr pellet method. FTIR measurements were carried out to identify the possible biomolecules responsible for the reduction and capping of Ag ions.

3. Results and Discussion

3.1 Visual Observation

After addition of peel extracts of pomegranate, banana, orange, tangerine and lemon to silver nitrate the color of reaction mixtures turned to dark brown within 5 min, (fig. 2) indicating the formation of silver nanoparticles. The color change is due to excitation of surface plasmon resonance in the silver nanoparticles [14].

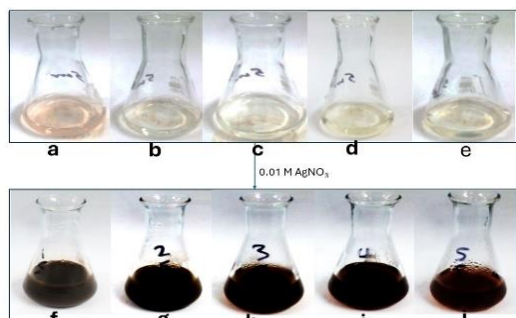


Figure 2. Change in color of the reaction mixture during synthesis of silver nanoparticles. Using silver nitrate solution (0.01M). a, pomegranate peel extract; b, banana peel extract; c, orange peel extract; d, tangerine peel extract; e, lemon peel extract; f, reaction mixture containing pomegranate peel extract; g, reaction mixture containing banana peel extract; h, reaction mixture containing orange peel extract; I, reaction mixture containing tangerine peel extract; j, reaction mixture containing lemon peel extract.

3.2 UV-Vis Spectroscopy

The formation of silver nanoparticles in aqueous solution was confirmed using UV-Vis spectrophotometer analysis. The strong surface plasmon resonance (SPR) band of AgNPs appears at the range of 440-480 nm [15]. Reaction mixtures of silver nitrate (0.01 M) with peel extracts of pomegranate, banana, orange, tangerine and lemon showed absorption peaks at 465,460,468,476 and 470 nm respectively which is specific to AgNPs.

3.3 Particle Size Analyzer (PSA)

Table 1 showed the mean of particle sizes produced using pomegranate, banana, orange, tangerine and lemon peel extracts. The smallest particle size was produced using pomegranate peel (9.5 nm) while the largest particle size was produced using orange peel (391.3 nm).

Table 1: Sizes of AgNPs produced using various fruit peel extracts

| +S.N. | Plant extract used | Mean particle size (nm) |
|-------|--------------------|-------------------------|
| 1 | Pomegranate peel | 9.5 |
| 2 | Banana peel | 16.2 |
| 3 | Orange peel | 391.3 |
| 4 | Tangerine peel | 68.3 |
| 5 | Lemon peel | 25.1 |

3.4 X-ray Diffraction (XRD) Pattern of the Synthesized Nanoparticles

The XRD patterns of synthesized AgNPs are shown

in (fig. 3). AgNPs synthesized from different plant extracts showed four distinct diffraction peaks at 38.06 °, 44.26 °, 64.5 ° and 77.30 °.

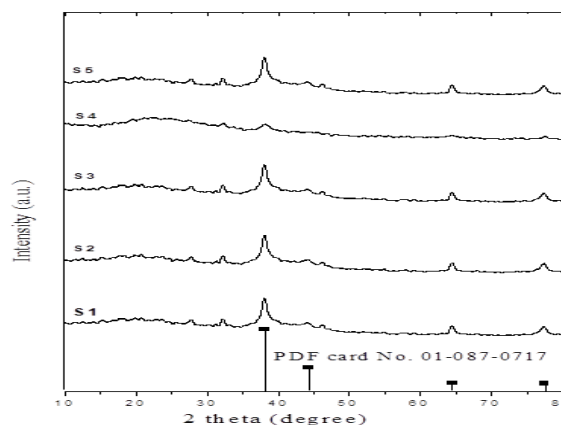


Figure 3. XRD pattern of AgNPs synthesized using different plant extracts. S1, pomegranate peel extract; S2, banana peel extract; S3, orange peel extract; S4, tangerine peel extract; S5, lemon peel extract.

3.5 SEM Analysis of the Synthesized Nanoparticles

The SEM characteristics of the synthesized AgNPs are shown in (fig. 4). Illustration of SEM showed somewhat spherical shaped nanoparticles. It indicates the completion of the nanoparticles synthesis process.

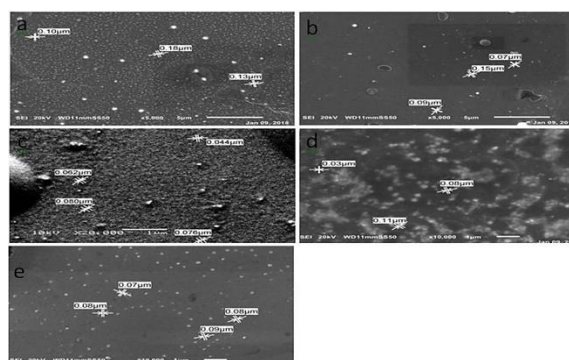


Figure 4. SEM micrographs of AgNPs synthesized using different plant extracts. a, pomegranate peel extract; b, banana peel extract; c, orange peel extract; d, tangerine peel extract; e, lemon peel extract.

3.6 FTIR

Results of FTIR study of biosynthesized AgNPs using pomegranate peel extract showed absorption peaks at 3767.1, 3398.69, 2926.11, 2112.12, 1708.99, 1383.01, 1055.1 and 572.88 cm^{-1} (fig. 5.a). The absorption peaks were assigned to free hydroxyl of alcohol or phenol, O-H of alcohol or N-H of amines, C-H of alkanes, O-C stretching, C=O of carboxylic acid or ester, hydroxyl groups or phenolic hydroxyl, C-N of aliphatic amines or alcohol/phenol and aromatic C-H respectively [11].

Results of FTIR study of biosynthesized AgNPs using banana peel extract showed absorption peaks at

3747.81, 3431.48, 2941.54, 2164.2, 1718.63, 1629.9, 1379.15 and 1049.31 cm^{-1} (fig. 5.b) . The absorption peaks were assigned to free hydroxyl of alcohol or phenol, O–H of alcohol or N–H of amines, C–H of alkanes, O–C stretching, C=O of carboxylic acid or ester, N–C=O of amide, hydroxyl groups or phenolic hydroxyl and C–N of aliphatic amines or alcohol/phenol respectively [11].

Results of FT-IR study of biosynthesized AgNPs using orange peel extract showed several peaks at 3878.98, 3417.98, 2924.18 , 2125.63, 1645.33, 1384.94 , 1059.96 and 557.45 cm^{-1} (fig.5.c) . The absorption peaks were assigned to O–H stretch of alcohol or phenol, O–H of alcohol or N–H of amines, C–H of alkane, O–C stretching, N–C=O of amide, hydroxyl groups or phenolic hydroxyl, C–N of aliphatic amines or alcohol/phenol and aromatic C–H respectively [11].

Results of FTIR study of biosynthesized AgNPs using tangerine peel extract showed several peaks at 3888.62, 3402.33, 2922.25, 2098.62, 1643.41, 1381.08 , 1251.84,1049.31 and 561.3 cm^{-1} (fig. 5.d) . The absorption peaks were assigned to O–H stretch of alcohol or phenol, O–H of alcohol or N–H of amines, C–H of alkanes, O–C stretching, N–C=O of amide, hydroxyl groups or phenolic hydroxyl, poly phenols, C–N of aliphatic amines or alcohol/phenol and aromatic C–H respectively [11].

Results of FT-IR study of biosynthesized AgNPs using lemon peel extract showed several peaks at 3890.55, 3421.83 , 1658.84, 1383.01, 1228.7, 1053.96 and 557.45 cm^{-1} (fig. 5.e). The absorption peaks were assigned to O–H stretch of alcohol or phenol, O–H of alcohol or N–H of amines, N–C=O of amide, hydroxyl groups or phenolic hydroxyl, poly phenols ,C–N of aliphatic amines or alcohol/phenol and aromatic C–H respectively [11].

Results of FT-IR study are summarized in (Table 2). The FT-IR results imply that the carboxyl (–C=O), hydroxyl (–OH) and amine (–NH) groups in plant extracts are mainly involved in fabrication of AgNPs.

Table 2: FTIR assignments of produced AgNPs using various fruit peel extracts

| Pomegranate peel | Wave number (cm^{-1}) | | | | Spectral assignments |
|------------------|----------------------------------|-------------|----------------|------------|---|
| | Banana peel | Orange peel | Tangerine peel | Lemon peel | |
| | | 3878.98 | 3888.62 | 3890.55 | O–H stretch of alcohol or phenol |
| 3767.1 | 3747.81 | | | | free hydroxyl of alcohol or phenol |
| 3398.69 | 3431.48 | 3417.98 | 3402.33 | 3421.83 | O–H of alcohol or N–H of amines |
| 2926.11 | 2941.54 | 2924.18 | 2922.25 | | C–H of alkanes |
| 2112.12 | 2164.2 | 2125.63 | 2098.62 | | O–C stretching |
| 1708.99 | 1718.63 | | | | C=O of carboxylic acid or ester |
| | 1629.9 | 1645.33 | 1643.41 | 1658.84 | N–C=O of amide |
| 1383.01 | 1379.15 | 1384.94 | 1381.08 | 1383.01 | hydroxyl groups or phenolic hydroxyl |
| | | | 1251.84 | 1228.7 | poly phenols |
| 1055.1 | 1049.31 | 1059.96 | 1049.31 | 1053.96 | C–N of aliphatic amines or alcohol/phenol |
| 572.88 | | 557.45 | 561.3 | 557.45 | aromatic C–H |

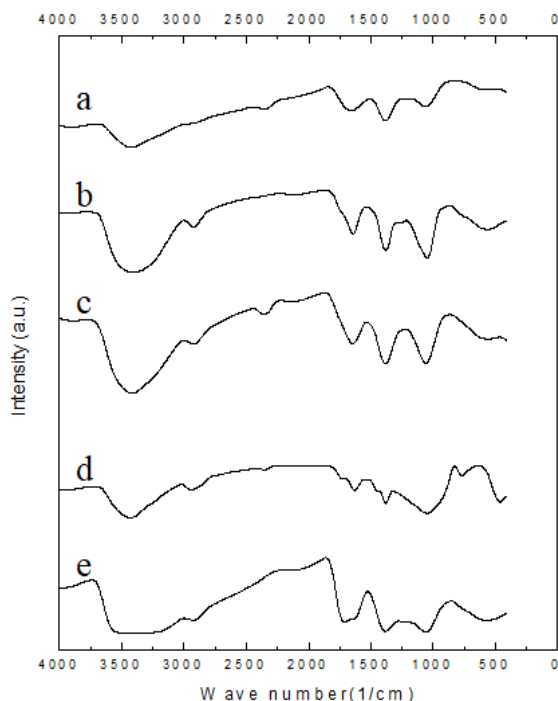


Figure 5. FTIR spectrum of particles synthesized using different plant extracts a, pomegranate peel extract; b, banana peel extract; c, orange peel extract; d, tangerine peel extract; e, lemon peel extract.

4. Conclusion

Pomegranate, banana, orange, tangerine and lemon peels as agricultural food waste materials were successfully utilized for the green, quick, simple, cost-effective and non-toxic synthesis of AgNPs. Plant extract acts as reducing, capping and stabilizing agents so there is no need for external toxic reducing agents. This method supports the dual purpose of agricultural food waste management.

5. References

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