

# Green synthesis, characterisation of silver nanoparticles and its photocatalytic activity from fruits extracts of *Actinidia deliciosa*, *Citrus sinensis*, *Phyllanthus emblica*, *Tamarindus indica*

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## Abstract

In comparison to physical and chemical approaches, the green synthesis of AgNPs using plant extracts is non-toxic to organisms, inexpensive, and good for the environment. In this study, we have successfully synthesised AgNPs utilising water-based fruit extracts from a variety of plants, such as *Actinidia deliciosa*, *Citrus sinensis*, *Phyllanthus emblica*, *Tamarindus indica* by adjusting the pH, precursor concentration, and extract volume allowed for the optimisation of the synthesis. By observing colour changes in the reaction mixture and quantifying them using UV-Vis spectroscopy, which showed extinction peaks for surface plasmon resonance around 407-417 nm, the synthesis of AgNPs was identified. (Yasmin et al., 2020; Giri et al., 2022). Analysis was carried out utilising XRD, IR, FESEM, and EDX to a high level of detail. The XRD study proved that the AgNPs had a face-centred cubic structure with average diameters ranging from 24 to 35 nanometers [(Asif et al., 2022). Transmission electron micrographs determined them to be spherical nanoparticles [Giri et al., 2022].

According to FESEM micrographs, the AgNPs have a spherical shape and a size distribution of 10 to 50 nm (Asif et al., 2022), suggesting that they could have many different uses. FTIR research studies revealed the functional group of the molecules derived from plant extracts. Using methyl orange (MO) as a model dye and subjecting the synthesised AgNPs to UV-Vis light, their photocatalytic activity was assessed. Within 120 minutes, the AgNPs degraded up to 95% of MO, demonstrating their exceptional photocatalytic effectiveness. The improved photocatalytic efficiency is explained by the plasmonic effect of AgNPs, which lowers the oxidation state of silver nanoparticles and increases the formation of reactive oxygen species. The excellent photocatalytic activity of AgNPs produced through green synthesis has shown to be a promising molecule that can be used in dye degradation and environmental remediation. As a future prospect, the molecule could also be used to check its efficiency in waste water treatment procedures. This study gives details of plant assisted synthesis by demonstrating its potential as a sustainable method to create AgNPs with acceptable features for many applications.

**Keywords:** *Actinidia deliciosa*, *Citrus sinensis*, *Phyllanthus emblica*, *Tamarindus indica*, Green synthesis, Silver nanoparticles (AgNPs), Photocatalytic activity, Nanotechnology

## Introduction

The production of silver nanoparticles (AgNPs) using plant extracts has recently attracted a lot of interest because it is a sustainable, economical, and biocompatible option (Giri et al., 2022; Asif et al., 2022). Bypassing the usage of harmful solvents and harsh reducing agents, plant-mediated synthesis of AgNPs has various benefits over traditional physical and chemical approaches (Mustapha et al., 2022). Asif et al. (2022) and Ajay et al. (2022) found that plant extracts containing different phytochemicals could be used in the green synthesis of AgNPs to reduce silver ions (Ag<sup>+</sup>) in a precursor solution, like silver nitrate (AgNO<sub>3</sub>). According to Giri et al. (2022), Ali et al. (2023), and Vanlalveni et al. (2021), a variety of phytochemicals such as enzymes, proteins, amino acids, vitamins, polysaccharides, and organic acids can be used as reducing agents and stability agents to help produce and stabilise AgNPs. The synthesis of AgNPs has been investigated using a broad range of plant components, such as leaves, flowers, seeds, barks, fruits, and roots (Da Silva et al., 2021; Sharma et al., 2022). Critical to the physiochemical and functional characteristics of the resultant AgNPs are their size, shape, and stability, all of which are affected by the plant material chosen (Asif et al., 2022; Prasad, 2014; Alex et al., 2020).

Asif et al. (2022), Ghoshal and Singh (2022), and Liaqat et al. (2022) observed that UV-Vis spectroscopy, X-ray diffraction (XRD), Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier-transform infrared spectroscopy (FTIR) are examples of analytical techniques commonly used to characterise the synthesised AgNPs.

These characterisation procedures give information about the AgNPs' composition, structure, and morphology. Using AgNPs generated from plants as photocatalysts to degrade organic contaminants, including dyes, in wastewater treatment is an intriguing prospect (Banerjee et al., 2014; Jaison & Sebastian, 2023). AgNPs possess distinct optical and electronic characteristics, including their surface plasmon resonance (SPR) effect, which amplifies their capacity to produce reactive oxygen species (ROS) when exposed to light. This property enables them to efficiently break down a wide range of organic pollutants (Asif et al. 2022; Vanlalveni et al. 2021).

The formation of AgNPs from fruits of a variety of selected plant extracts was detailed in this study, along with their thorough characterization and assessment of their photocatalytic activity in the degrading of organic dyes. This study emphasizes the significance of using AgNPs produced by green synthesis in cleaning of polluted environments.

#### Material and Methods:

##### Materials:

Silver nitrate ( $\text{AgNO}_3$ ) was procured from Sisco Research Laboratory, Mumbai, India. All other chemicals and reagents used were of highly pure analytical grade. Fruits of *Actinidia deliciosa*, *Citrus sinensis*, *Phyllanthus emblica*, *Tamarindus indica*, were collected from Maval, Mulshi, Pune region.

##### Preparation of plant extract:

The fruits collected from *Actinidia deliciosa*, *Citrus sinensis*, *Phyllanthus emblica*, *Tamarindus indica* were washed thoroughly with distilled water several times to remove dust and dried under shade. The extract was prepared from well-dried and powdered sample, then it was dissolved in distilled water and stirred for 30 min at 50–60°C. It was then kept at 4°C for further analysis as shown in Figure 1.

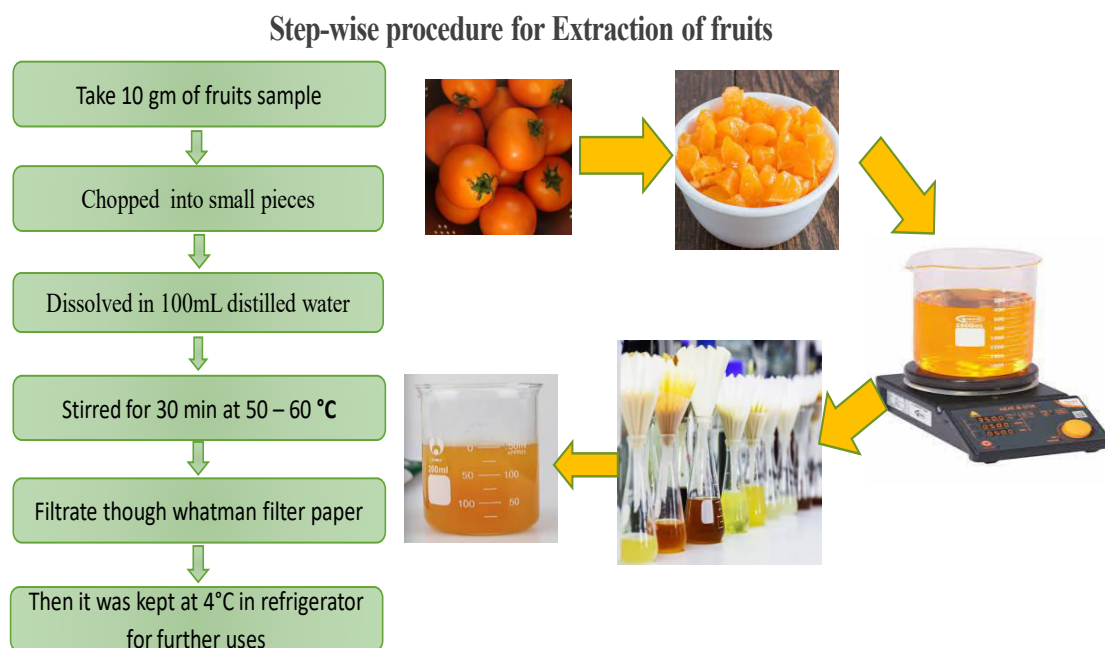
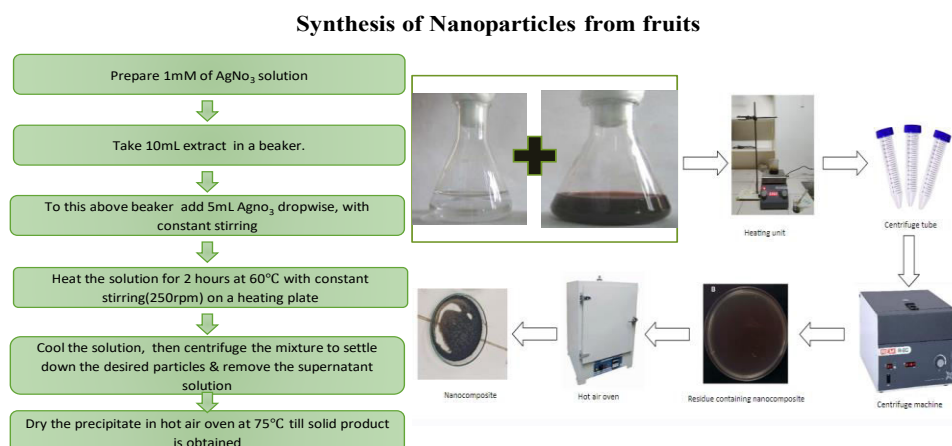


Fig- Step-wise procedure for Extraction

Figure 1: Step wise extraction procedure

##### Synthesis of Silver (AgNPs):

The silver nitrate was dissolved in 1000 ml deionised water to obtain a concentration of 1mM  $\text{AgNO}_3$ . The freshly prepared Silver nitrate solution was then added to the fruit extract obtained from the selected plants and was kept at constant stirring. The mixture was heated at 60–70°C. Change in color from yellow to brown was observed after 25–30 min as shown in Figure 2 and this confirmed the formation of silver nanoparticles.

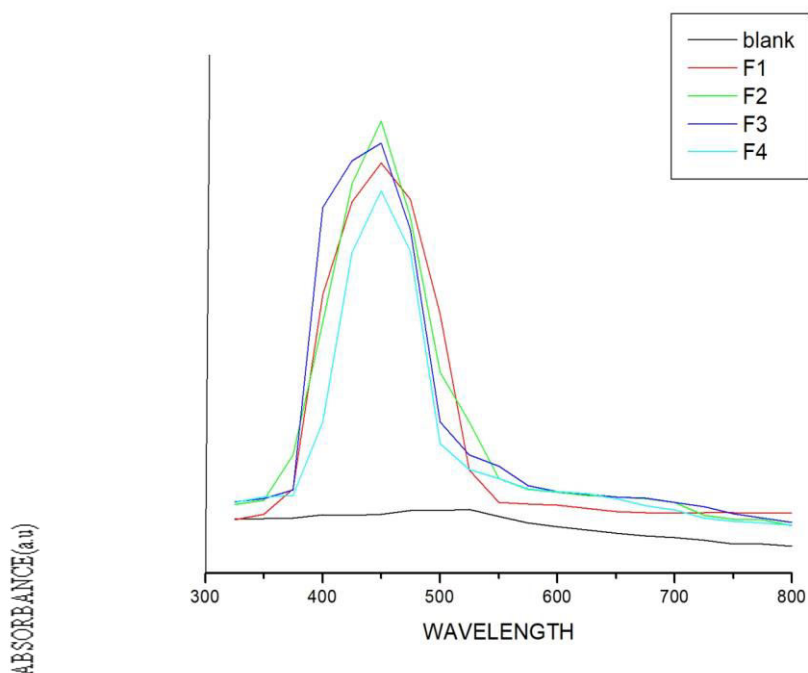


**Figure 2: Synthesis of nanoparticles from fruits**

### Characterization:

After synthesizing silver nanomaterials by precipitation methods, characterisation activities were undertaken for further investigations. Furthermore, the study explored the influence of different precursors and experimental parameters such as temperature and duration on the physicochemical properties of the synthesized materials. The study also provides an overview of characterization techniques including UV-DRS, FTIR, XRD, particle size analysis, and FESEM that highlights the significance of the physicochemical analysis of synthesized Silver nanomaterials.

### 1. UV-Vis SPECTROSCOPY



**Figure 3: UV-Visible spectra of AgNPs from Fruit extracts of Kiwi (F1), Orange (F2), Amla (F3) and Tamarind (F4)**

Silver nano particle was characterized by UV–visible absorption spectroscopy as shown in Figure 3. The UV–visible absorption spectra of the prepared AgNPs dispersed in water solution and scanned in the wavelength between 200–800nm ranges for fruits samples, showed the maximum absorbance at 450 nm as seen in Figure 3 and the energy band gap of AgNPs was found to be at 425 nm at 2.92 eV as shown in Table:1.

**Table 1: Band gap from UV-Vis Spectroscopy studies**

| Sample | Max Wavelength(nm) | Band gap energy(eV) |
|--------|--------------------|---------------------|
| F1     | 425                | 2.92                |
| F2     | 425                | 2.92                |
| F3     | 450                | 2.76                |

|    |     |      |
|----|-----|------|
| F4 | 450 | 2.76 |
|----|-----|------|

## 2. XRD spectra of AgNPs

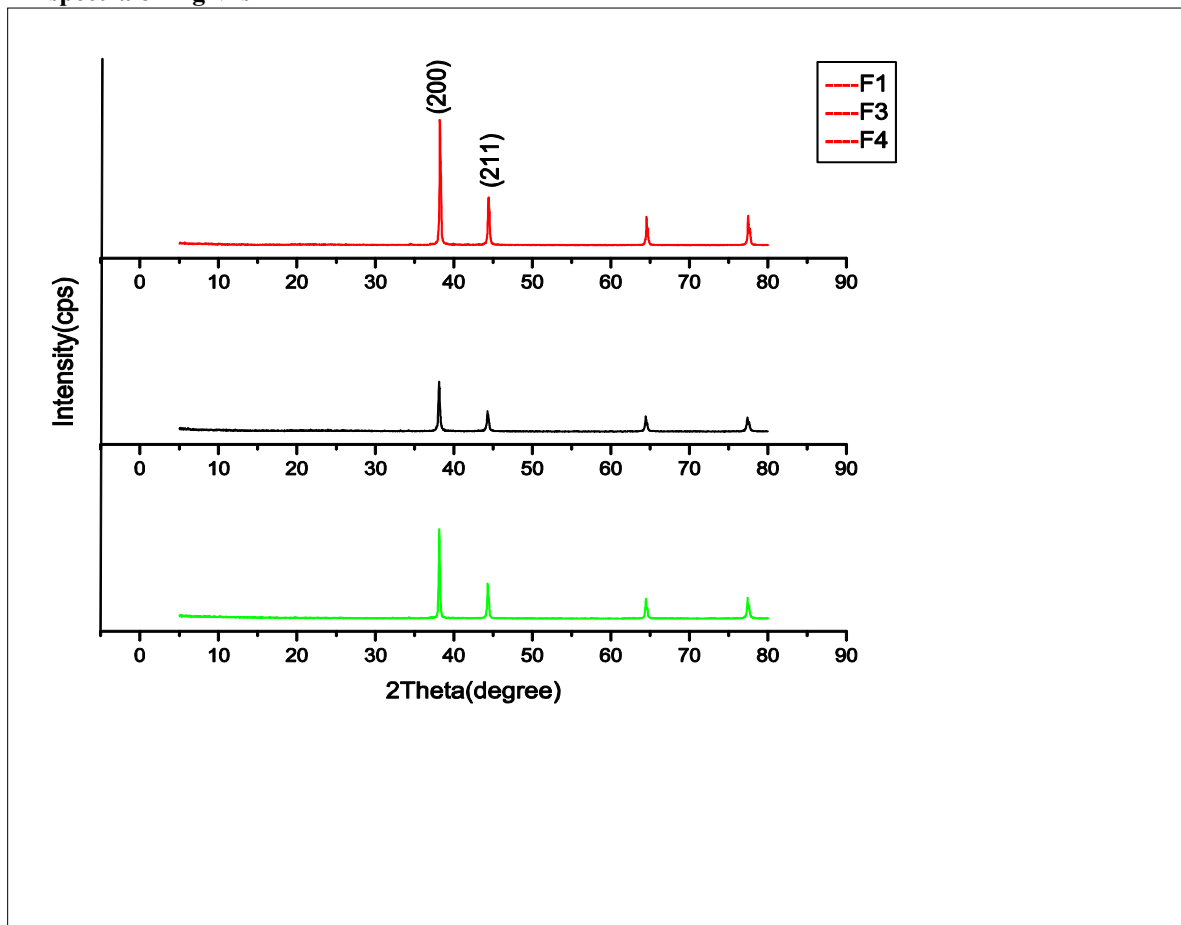


Figure 4: XRD spectra of AgNPs from Fruit extracts of Kiwi (F1), Orange (F2), Amla (F3), Tamarind (F4). AgNPs calcinated at 600°C showed XRD peaks as seen in Figure 4 at  $2\theta=33.155, 35.645, 40.865, 43.975, 49.535, 54.185, 62.465, 64.055$  which are in accordance to crystal planes of the AgNPs and indexed to (220), (311), (222), (400), (331), (422), (511), (531), and (442), respectively. Other low intensity peaks were also observed. All peaks, including high and low intensity peaks correlated with standard JCPDS file No. 04-0783. The average crystallite size was estimated to be 10.01 nm calculated using Debye-Scherrer's formula. The sharp peaks suggested that silver nanoparticles are crystallized well enough to be detected.

## 3. FT-IR:

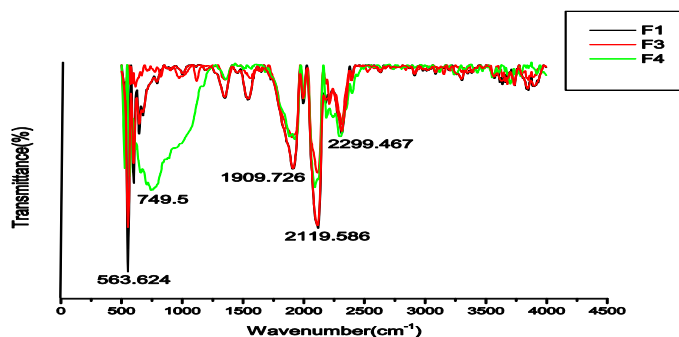


Figure 5: FTIR spectra of AgNPs from Fruit extracts of Kiwi (F1), Orange (F2), Amla (F3), Tamarind (F4)

The spectral data recorded revealed two types of vibrations (i.e., stretching and bending) in the wavelength range of 4,000 to 500  $\text{cm}^{-1}$ . The presence of band was observed at 2119 and 2299 stretching vibration at planar region. Several C-N stretching vibration peaks at 1132, 1098 1058 were observed as shown in Figure 5. In addition, the presence of bands at 1380  $\text{cm}^{-1}$  and 1280  $\text{cm}^{-1}$  in the FT-IR spectra suggested that the capping agent of green synthesized nanoparticles possesses an aromatic amine groups with specific signatures of amide linkages between amino acid residues in the proteins at the infrared region of the electromagnetic spectrum, as reported by Shaligram et al, while the stretching frequency 1909  $\text{cm}^{-1}$  belongs to aromatic carbonyl frequency which act as stabilizing agent on the surface of AgNPs.

#### 4. FESEM images and E-Dax of AgNPs

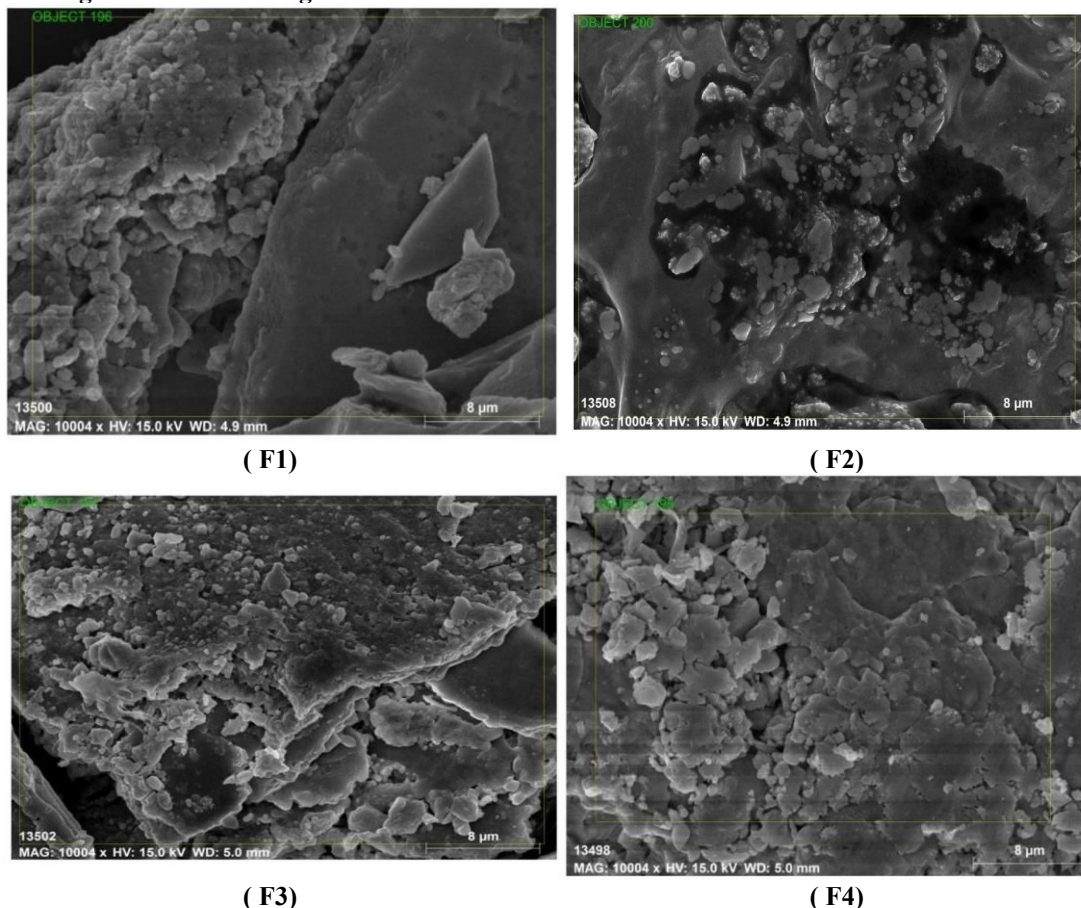


Figure 6: FESEM of AgNPs from Fruit extracts of Kiwi (F1), Orange (F2), Amla (F3), Tamarind(F4)

**EDS Report**

Spectrum: OBJECT 196

| El     | AN | Series   | unm.    | C norm. | C Atom. | C Error (1 Sigma) |
|--------|----|----------|---------|---------|---------|-------------------|
|        |    |          | [wt. %] | [wt. %] | [at. %] | [wt. %]           |
| Ag     | 47 | L-series | 61.16   | 76.36   | 31.34   | 1.95              |
| O      | 8  | K-series | 13.81   | 17.25   | 47.73   | 2.18              |
| N      | 7  | K-series | 3.99    | 4.97    | 15.73   | 0.80              |
| C      | 6  | K-series | 1.13    | 1.42    | 5.22    | 0.27              |
| Au     | 79 | M-series | 0.00    | 0.00    | 0.00    | 0.00              |
| Total: |    |          | 80.09   | 100.00  | 100.00  |                   |

**EDS Report**

Spectrum: OBJECT 201

| El     | AN | Series   | unm.    | C norm. | C Atom. | C Error (1 Sigma) |
|--------|----|----------|---------|---------|---------|-------------------|
|        |    |          | [wt. %] | [wt. %] | [at. %] | [wt. %]           |
| Ag     | 47 | L-series | 46.55   | 69.95   | 24.78   | 1.49              |
| O      | 8  | K-series | 10.79   | 16.22   | 38.68   | 1.69              |
| C      | 6  | K-series | 6.10    | 9.16    | 29.09   | 0.91              |
| Al     | 13 | K-series | 1.71    | 2.57    | 3.63    | 0.11              |
| H      | 1  | K-series | 0.81    | 1.22    | 3.33    | 0.27              |
| Cu     | 29 | K-series | 0.59    | 0.89    | 0.53    | 0.08              |
| Au     | 79 | M-series | 0.00    | 0.00    | 0.00    | 0.00              |
| Total: |    |          | 66.55   | 100.00  | 100.00  |                   |

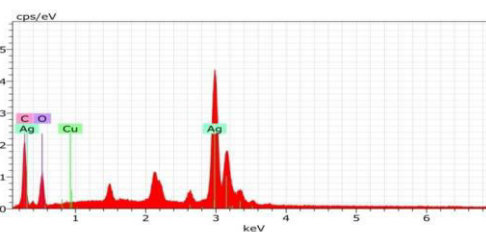
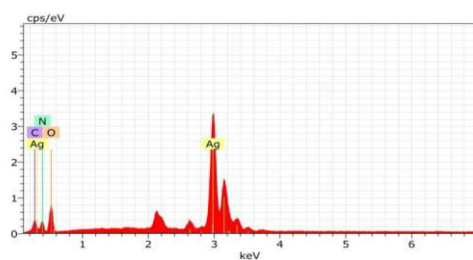


Figure 7 a : EDS analysis F1

**EDS Report**

Spectrum: OBJECT 197

| El     | AN | Series   | unn.   | C norm. | C Atom. | C Error | (1 Sigma) |
|--------|----|----------|--------|---------|---------|---------|-----------|
|        |    |          | [wt.%] | [wt.%]  | [at.%]  |         | [wt.%]    |
| Ag     | 47 | L-series | 52.66  | 71.19   | 26.10   |         | 1.68      |
| O      | 8  | K-series | 13.69  | 18.51   | 45.76   |         | 2.08      |
| N      | 7  | K-series | 3.52   | 4.76    | 13.43   |         | 0.71      |
| C      | 6  | K-series | 2.67   | 3.61    | 11.87   |         | 0.48      |
| Al     | 13 | K-series | 1.43   | 1.94    | 2.84    |         | 0.10      |
| Au     | 79 | M-series | 0.00   | 0.00    | 0.00    |         | 0.00      |
| S      | 16 | K-series | 0.00   | 0.00    | 0.00    |         | 0.00      |
| Total: |    |          | 73.97  | 100.00  | 100.00  |         |           |

Figure 7 b : EDS analysis F2

**EDS Report**

Spectrum: OBJECT 195

| El     | AN | Series   | unn.   | C norm. | C Atom. | C Error | (1 Sigma) |
|--------|----|----------|--------|---------|---------|---------|-----------|
|        |    |          | [wt.%] | [wt.%]  | [at.%]  |         | [wt.%]    |
| Ag     | 47 | L-series | 54.40  | 72.64   | 27.09   |         | 1.79      |
| O      | 8  | K-series | 14.70  | 19.63   | 49.37   |         | 2.85      |
| N      | 7  | K-series | 3.66   | 4.89    | 14.04   |         | 1.02      |
| C      | 6  | K-series | 2.12   | 2.84    | 9.50    |         | 0.56      |
| Au     | 79 | M-series | 0.00   | 0.00    | 0.00    |         | 0.00      |
| S      | 16 | K-series | 0.00   | 0.00    | 0.00    |         | 0.00      |
| Total: |    |          | 74.89  | 100.00  | 100.00  |         |           |

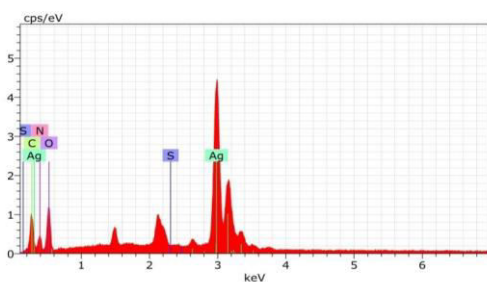


Figure 7 c : EDS analysis F3

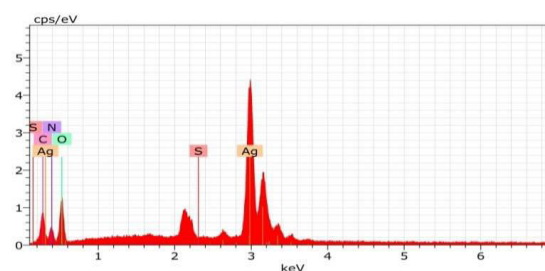


Figure 7 d : EDS analysis F4

Figure 7 (a,b,c,d) : EDX spectrum of AgNPs with a higher percentage of the silver nanoparticle

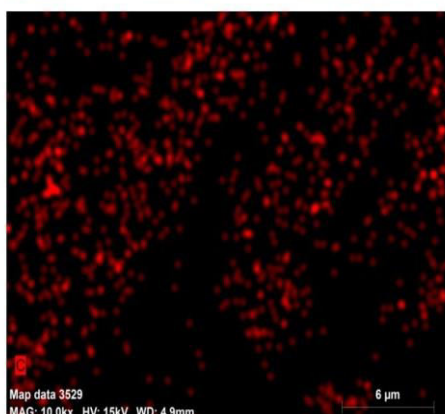
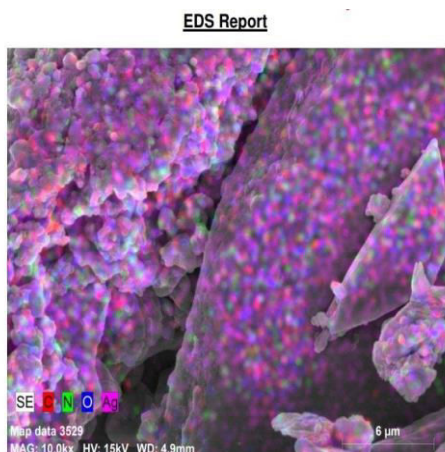


Figure 8a : Elemental composition by EDS-F1

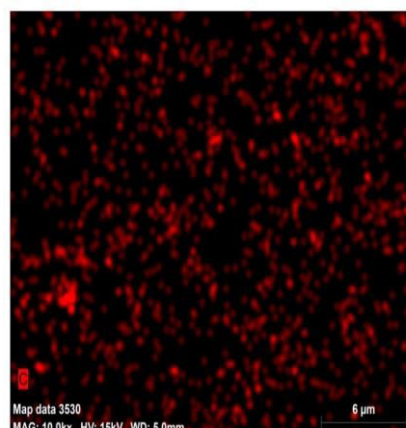
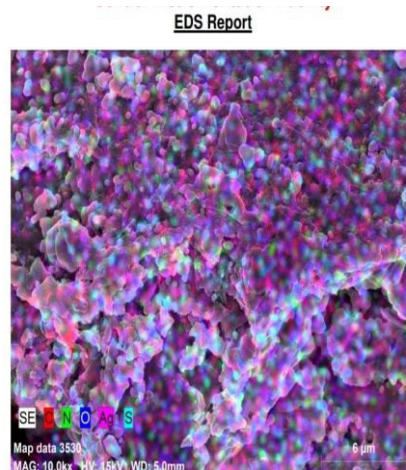


Figure 8b : Elemental composition by EDS-F2

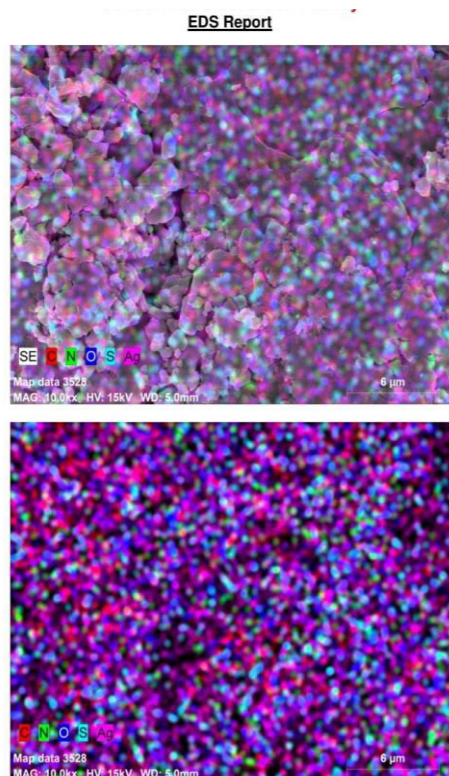


Figure 8c : Elemental composition by EDS-F3

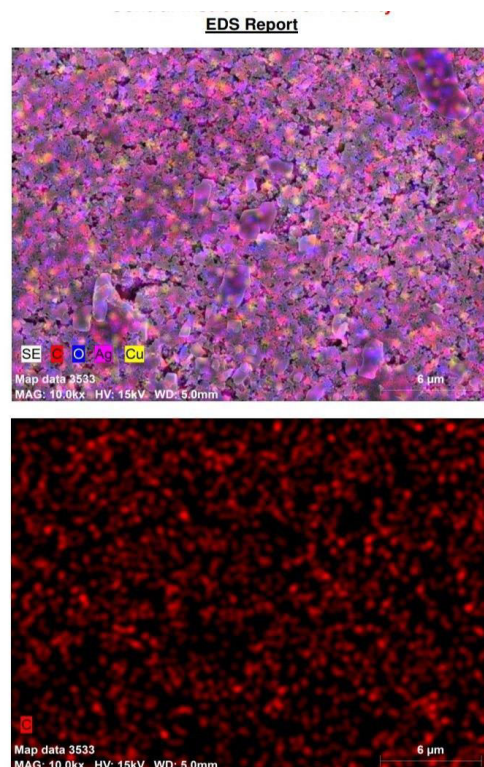


Figure 8d : Elemental composition by EDS-F4

The E-DAX analysis provides information about elemental composition of AgNPs from selected fruits and it confirms the presence of the element silver in the ratio ranging between 40 to 80%.

#### Application:

**Photocatalytic degradation.** The photocatalytic activity of silver nanoparticle was analyzed by photo degradation of methyl orange dye as a model. An additional vital application of silver nanoparticle is in the domain of photocatalytic degradation, which has become an ever more effective, ecofriendly with low cost to eliminate toxic organic materials from the ecosystem. Methyl orange is an anionic organic dye which has an azo ( $N=N$ ) and diethyl amine group and therefore, it is risky for livelihood and has to be degraded from the nature. In this study, the degradation activity of synthesized nanomaterial was evaluated against methyl orange. The UV-vis absorbance peak of methyl orange dye at 460 nm is recorded.

The result of absorbance peak is gradually decreased with increasing period of 1hr incubation. The degradation was initiated by photons of sunlight striking on the surface of silver nanoparticle, and it results in the excitation of conduction of electrons on the surface of silver nanoparticle as a result of SPR effect. Therefore, this article is designed for degradation of organic dyes under visible light irradiation in the presence of biogenic nanoparticles, which is very stable and efficient photocatalysts.

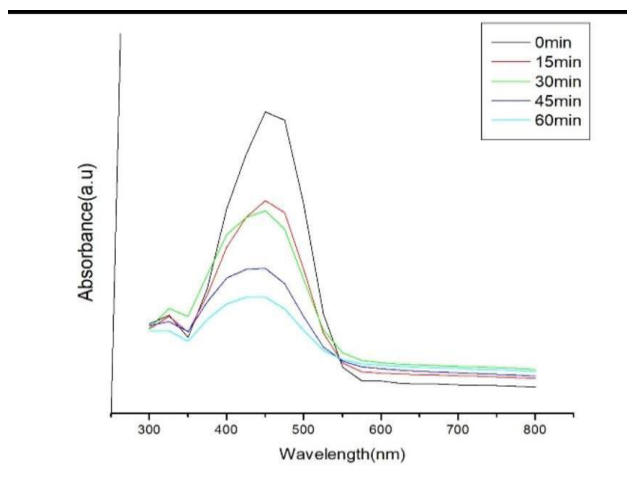


Figure 9a : Photocatalytic activity of F1

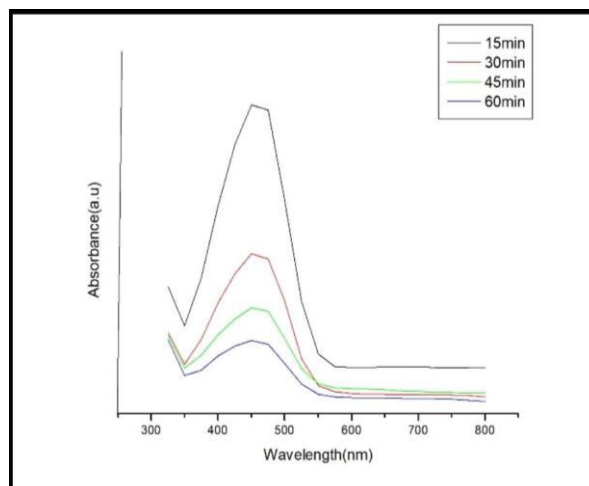


Figure 9b : Photocatalytic activity of F2

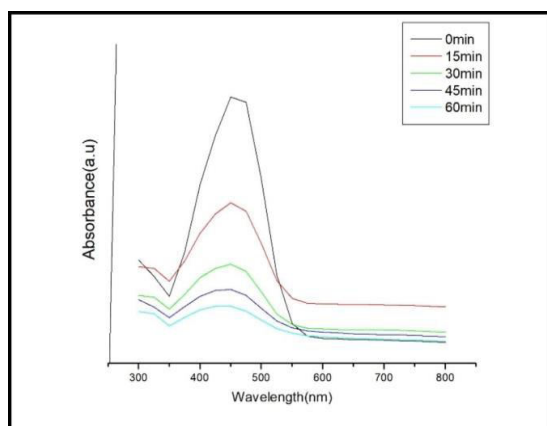


Figure 9c : Photocatalytic activity of F3

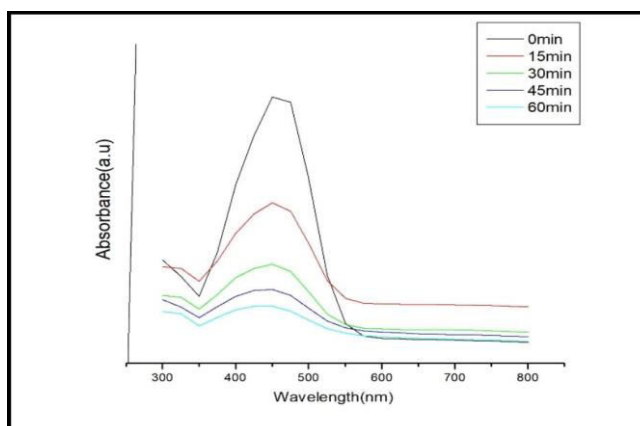


Figure 9d : Photocatalytic activity of F4

### Conclusion:

The green synthesis of silver nanoparticles (AgNPs) using plant extracts is a promising area due to its eco-friendliness, cost-effectiveness, and non-toxicity. This study synthesized AgNPs using aqueous fruit extracts from various plants such as *Actinidia deliciosa*, *Citrus sinensis*, *Phyllanthus emblica*, *Tamarindus indica*. The synthesis was optimized by changing pH, precursor concentration, and extract volume. The spherical morphology of AgNPs, with a size distribution between 10 and 50 nm, opens up potential applications in nanotechnology. The FTIR analysis revealed the presence of biomolecules from the plant extracts of *Actinidia deliciosa*, *Citrus sinensis*, *Phyllanthus emblica*, *Tamarindus indica* as capping and stabilizing agents. The AgNPs exhibited excellent photocatalytic efficiency with up to 95% degradation of methyl orange (MO) under UV-Vis light radiation. This study highlights the potential of plant-mediated synthesis as a sustainable approach to produce AgNPs with desirable properties for various applications.

The study synthesized silver nanoparticles from fruit extracts of *Actinidia deliciosa*, *Citrus sinensis*, *Phyllanthus emblica*, *Tamarindus indica*. The silver nitrate was dissolved in deionized water to create silver nanoparticles. The resulting silver nanoparticles characterized using UV-DRS, FTIR, XRD, particle size analysis, and FESEM. The XRD spectra showed sharp peaks, suggesting good crystallization. FT-IR spectra revealed two types of vibrations, stretching and bending, and indicated the capping agent of the green synthesized nanoparticles. The EDAX analysis confirmed the presence of silver in the ratio between 40 to 80%. The study highlights the significance of photocatalytic applications in the development of silver nanomaterials.

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