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RESEARCH ARTICLE

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SYNTHESIS AND CHARACTERISATION OF SILVER NANOPARTICLES FROM RICE FLATSEDGE [*CYPERUS IRIA* (L)] STEM EXTRACT

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ABSTRACT

The biosynthesis of nanoparticles has been proposed as a cost effective and environmental friendly alternative to chemical and physical methods. The present research explores a plant mediated synthesis of silver nanoparticles (SNPs) as a green chemistry approach that interconnects nanotechnology and plant biotechnology. It has been demonstrated using *Cyperus Iria* (L) stem n-hexane extract. The AgNPs were characterized by Ultraviolet-Visible spectrometer, Scanning electron microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX), Selected Area Diffraction Pattern (SAED), Fourier Transform infrared spectroscopy (FT IR) analysis was used to characterize the silver nanoparticles formed. TEM micrographs showed spherical particles with an average size of 32 nm. The XRD pattern showed the characteristic Bragg peaks suggested that the face center cubic (fcc) silver nanoparticles and confirmed that these nanoparticles are crystalline in nature.

Key words: *C.iria* stem extract, Nanoparticle synthesis, Characterisation, antimicrobial study

1. Introduction

Green synthesis of silver nanoparticles is evolving into an important branch of nanotechnology. Plant based synthesis of silver nanoparticles is gaining more importance owing to its simplicity, rapid rate of synthesis of nanoparticles (NPs) of attractive and diverse morphologies and elimination of elaborate maintenance of cell cultures and Eco friendliness. It has many advantages such as, ease with which the process can be measured up, economic viability and etc. Presently, the researchers are looking into the development of cost-effective procedures for producing reproducible, stable and biocompatible metal NPs. Aluminum, Gold, Zinc, Carbon, Titanium, Palladium, Iron and Copper have been routinely used for the synthesis of NPs. Metal nanoparticles are of use in various catalytic applications, electronics, biology and biomedical applications, material science, physics, environmental remediation fields[1].

Presently available literature revealed that the metal NPs synthesis using plants, microorganisms and algae as source has been unexplored and underexploited. Resistance to antimicrobial agents by pathogenic bacteria has emerged in recent years and is a major health problem. The development of green processes for

the synthesis of NP is evolving into an important branch of green nanotechnology. Plants have evolved in the presence of natural nanomaterials. A variety of preparation routes have been reported for the preparation of silver nanoparticles. Silver salt reduction was the most used[3,5].

Cyperus Iria L. (Family: Cyperaceae) commonly known as Rice flatsedge] grows well in moist to wet soil in annual and plantation crops. It is one of the most common weed in rice fields and other flooded crops. It is found nearly everywhere in irrigated rice fields. The stem is full, trigonal, thin, smooth, non-winged angles, 1 to 2 mm in diameter and 10 to 50 cm high (figure 1). *C. iria* contains a high concentration of juvenile hormone (JH) III, which plays important biological role(s) in the plant mechanism perhaps through plant-insect, plant-plant or other interactions. In our current study, the silver nanoparticles have been synthesized using screened extract of the rice flatsedge plant stem and report that silver nanoparticles can be applied effectively in the control of microorganisms and the prevention of deleterious infections.

2. Materials and Method

All chemicals and reagents had analytical grade. Silver nitrate, n-hexane with high purity purchased from Sd Fine/Merck India Chemicals, India.

2.1 Apparatus and Instruments: The conventional Soxhlet extraction apparatus was used, which consists of a condenser, a Soxhlet chamber, and an extraction flask. The extractor thimble was permeable one with 44 mm internal diameter and 200 mm external length. The rotary evaporator was used for evaporation of solvent of extracted material.

2.2 Sampling and extraction: The fresh sample of *Cyperus Iria* (L) stem powder was collected at the end of September 2013 in local agricultural fields (Giddaluru revenue sub-division). The plant material was completely dried in sunlight and cut into small pieces, ground in grinding mill with particle size of less than 2 mm (Figure 1). The raw grinded sample was sealed and stored in desiccators for further usage. 30gm homogenized *Cyperus Iria* (L) stem sample was extracted with 500 ml n-hexane for 2hour. The extraction was repeated for 3 times and then the extracts were filtered through whatman filter paper no 42. Then the filtered extract was stored in refrigerator at 4°C for further use in synthesis of silver nanoparticles.

2.3 Synthesis of AgNPs (SNPs): The synthesis of silver nanoparticles was done by mixing *C.iria* (L) stem extract and 1 mM of aqueous silver nitrate solution ($AgNO_3$) in the ratio 1:20 added to plant extract ethanolic solution and heated at 80 ± 2°C until the colour of the solution was changed from colour less to thick brown (Figure 2). Resulted solutions were settled for 24 hours in dark to avoid any further photochemical reactions, after that the solution was centrifuged at 5000 rpm for 10 minutes with magnetic shaker. The supernatant was discarded and the pellet was air dried in the incubator.

The bio reduction of Ag^+ ions was monitored by periodic sampling by the UV spectrophotometer. The AgNPs in the freeze-drying bottle were suspended in ultrahigh purity water for all characterization methods and antibacterial assays. During biosynthesis of silver nanoparticles when stem extract was added to 100 ml of 1 mM $AgNO_3$ salt, the ionization took place as follows:

$$AgNO_3\,(aq) \leftrightarrow Ag^+\,(aq) + NO_3^-(aq)$$

$$e^- + Ag^+ \rightarrow Ag^o$$

It is assumed that the silver ions enter inside the plant cell via the H^+ATPase protein embedded in the thylakoid membrane by an electro genic pump[4]. Synthesis of silver nanoparticles is a photochemical reduction reaction.

2.4 Characterization techniques

- UV–visible spectroscopy: The formation of dark brown color during the synthesis was confirmed as the formation of AgNPs. The reduction of the pure AgNPs was recorded under UV–visible spectroscopy using ELico model UV–visible spectrophotometer between 300 nm and 700 nm. The UV–visible spectra of the plant leaf extract and silver nitrate solution were also recorded.
- FTIR analysis was done using Perkin Elemer Spectrum-1, and was used to identify the chemical constituents in the region of 400-4000 cm^{-1} of the Ag-NPs

- XRD measurement: XRD measurements of Ag-NPs were cast into glass slides were done by Phillips PW 1830 instrument. The operating voltage of 40 kV and current of 30 mA with Cu kα radiation of 0.1541 nm wavelength, in the 2θ range 10- 80º, step size 0.02/θ.
- The morphology of the Ag-NPs was analyzed using an SEM. The powdered Ag-NPs were uniformly spread and sputter coated with platinum in an ion coater for 120 seconds, then observed by SEM JEOL-JSM 6360 MODEL, JAPAN). The size distribution of the nanoparticle was obtained by counting 150 particles from an enlarged SEM image.32 Elemental analysis of the powdered Ag-NPs was conducted using an EDX detector (EDS, EDAX Inc., Mahwah, NJ, USA) attached to the SEM machine.
- TEM analysis of Ag-NPs: Sample for TEM analysis was prepared, as mentioned in IR sample preparations. The sample was first sonicated (Vibronics VS 80) for 5 minutes. Ag-NPs were loaded on carbon coated copper grids, and solvent was allowed to evaporate under Infra light for 30 minutes. TEM measurements were performed on Phillips modle CM 20 instrument, operated at an accelerating voltage at 200 kV.

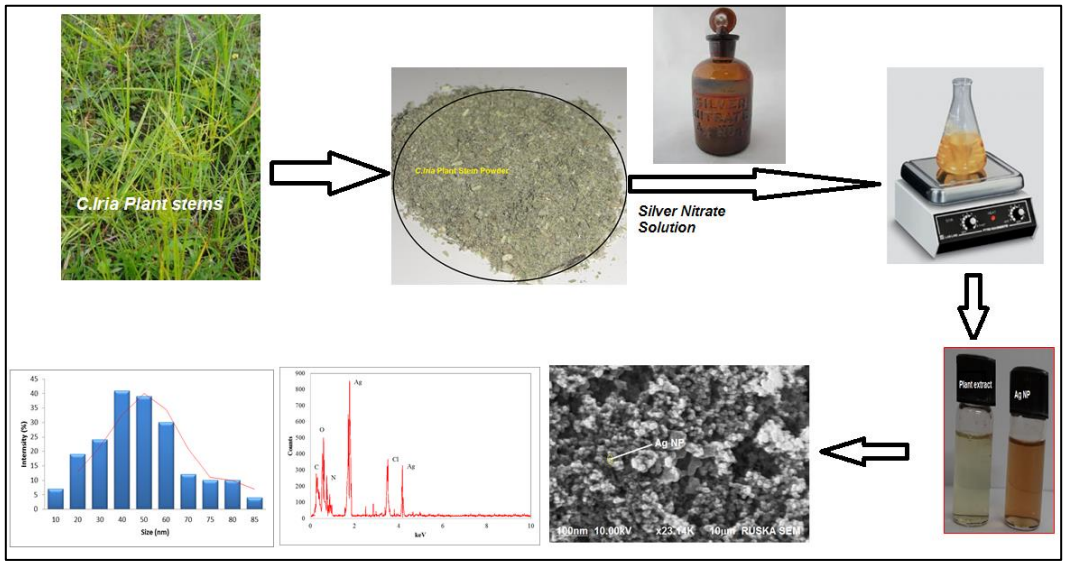

Figure 1. Graphical representation of green and chemical syntheses of silver nanoparticles (SNPs) using *C.ira* L stem and evaluation of their surface characteristics

3. RESULTS AND DISCUSSION

In the present study, n-hexane stem extract of *C.iria* was effectively used for the synthesis of SNPs. After treatment of aqueous plant leaf extract with 1mM $AgNO_3$ colour change was observed in the reaction mixture from light -green to dark- brown (Figure 1). It takes about 25-30 min to complete the reaction with the 5 min exposure to sunlight. The change in colour indicated the formation of SNPs which occurs due to excitation of surface plasma resonance in metal nanoparticles[8].

3.1. UV-Vis Spectrophotometric studies

It is well known that silver nanoparticles exhibit reddish brown colour in aqueous solution due to excitation of surface Plasmon vibrations in silver nanoparticles. Ag^{2+} ions of silver nitrate are found to be reduced to Ag atoms. It is generally recognized that UV-Vis spectroscopy could be used to examine size and shape controlled nanoparticles in aqueous suspensions. The formation of SNPs was investigated by UV-Vis spectroscopy technique. Absorption measurement was carried out using UV-Visible spectrophotometer at a resolution of 1 nm. The UV- Visible spectra of synthesized AgNPs showed absorption peak at 449.3 nm which is specific for SNPs. Obtained results showed good resemblance with many previous studies6,7. The UV- Visible spectra of AgNPs was shown in Figure 2.

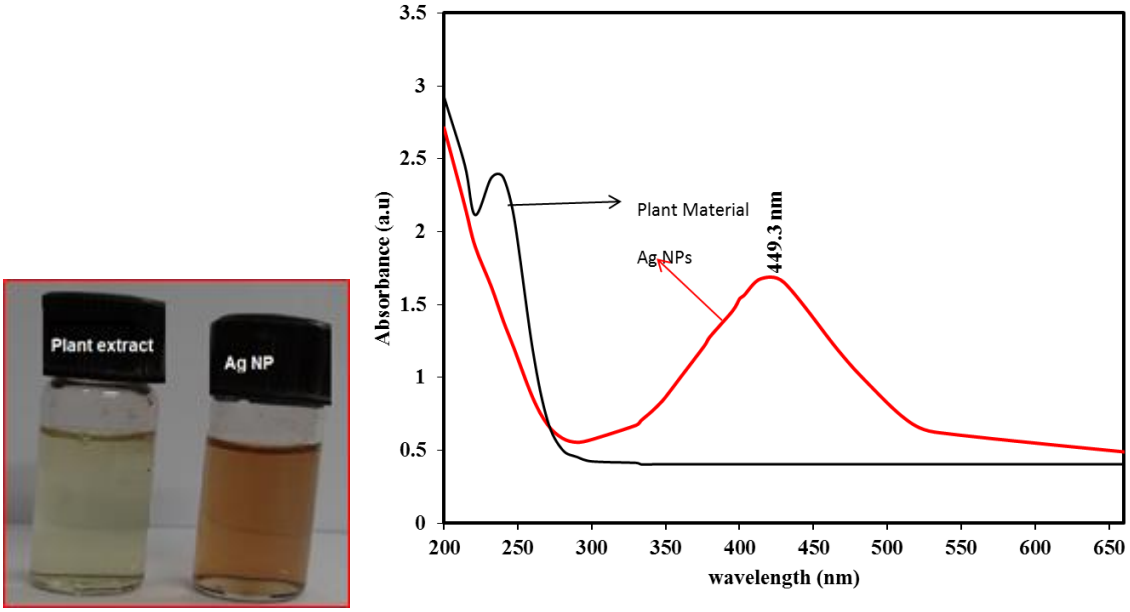

Figure 2: Silver nanoparticles before and after bio reduction (Ag^+ to Ag^o) (left); (b) UV absorption spectra of SNPs after bio reduction (right)

3.2 FT-IR Analysis

FT-IR study of SNPs was carried out to identify the possible biomolecules responsible for synthesis and stabilization of AgNPs. Spectra of pure *C.iria* L stem extract and chemically synthesized SNPs as shown in Figure 3.

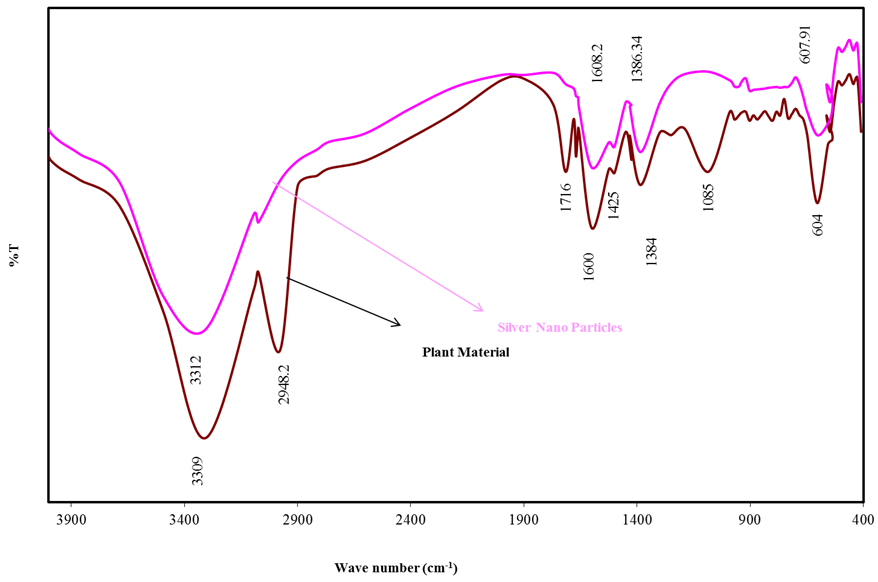

Figure 3: Comparison of the IR spectra of pure *C.iria* L stem extract and chemically synthesized SNPs

As shown in Figure 3, the FT-IR spectrum of pure *C.iria* L stem extract is remarkably similar to the FT-IR spectrum of SNPs, except slight minimal shifts in a few peaks. This striking resemblance between these two spectra clearly suggests that some of the residual phytomolecules of the S *C.iria* L stem remained attached on the surface of the synthesized SNPs. Therefore, the FT-IR spectrum of *C.iria* L stem exhibit several absorption peaks at different locations including at, 3309 cm^{-1} (due to alcoholic or phenolic-OH), ~2948 cm^{-1} (-C–H, asymmetrical stretch), ~1716 cm^{-1} (due to C=O stretch), The narrow peaks at 1600 and 1445 regions clearly evince the presence of stretches of C=C-C and C-H bonds in aromatic rings that are found in Coumaric acid,

Ferulic acid etc[9] 1384 cm^{-1} (C–O stretch) ~1085 cm^{-1} (C–O) which correspond to various oxygen containing functional groups. The peak at 604 cm^{-1} is corresponds the alcohol and OH out-of-plane bending. Majority of these peaks are also present in the IR spectrum of SNPs spectra with some minimal shifts. For instance, all the aforementioned peaks are slightly shifted in the IR spectrum of SNPs and appeared at ~3312 cm^{-1}, ~2946 cm^{-1}, ~1608 cm^{-1}, ~1386 cm^{-1}. Therefore, the presence of these peaks in the IR spectrum of SNPs clearly points towards the successful dual role of the *C.iria* L stem extract, both as a reducing and capping agent.

3.3 X-ray Diffraction al analysis

The diffractogram of SNPs exhibited five intense diffractions (Figure 4), which not only confirms the crystallinity of the sample but also established the identity of the NPs. In Figure 4 of XRD pattern is shown typically peaks at 19.7°, 33.8°, 38.2°, 63.6° and 78.1° corresponding to the (111), (200), (220), (311) and (222) diffractions for face centered cubic (fcc) silver phase (JCPS 04-0786), in a similar way as recently published by *laccase* Ag/AgCl nanoparticles synthesis or from *F. oxysporum*.

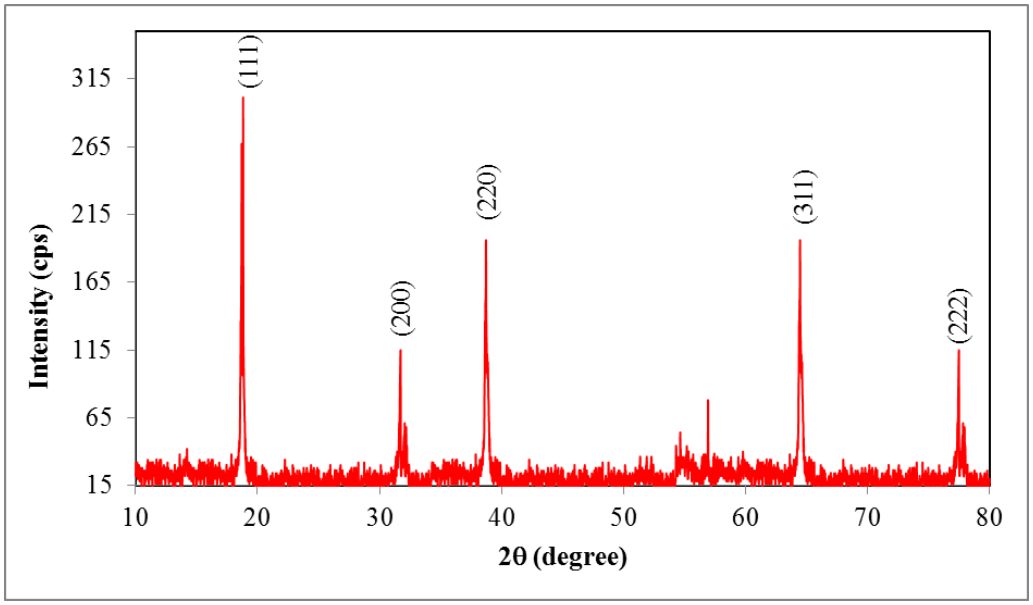

Figure 4: XRD patterns of SNPs synthesized by treating *C.Iria* L. extract with 1 mM silver nitrate

The unassigned peaks could be due to the crystallization of bioorganic phase that occurs on the surface of the nanoparticle. Two small insignificant impurity peaks observed at 50˚ and 60˚ are attributed to the presence of other organic substances in culture supernatant. The X-ray diffraction peaks were found to be broad around their bases indicating that the silver particles are in nanosizes. The peak broadening at half maximum intensity of the X-ray diffraction lines is due to a reduction in crystallite size, flattening and micro-strains within the diffracting domains[13].

3.4 SEM-EDX studies

SEM technique was employed to visualize the size and shape of silver nanoparticles. The SEM images of the AgNPs are shown in fig. 5. The formation of silver nanoparticles as well as their morphological dimensions in the SEM study demonstrated that the average size was from 32-35 nm with inter-particle distance. It is seen that AgNPs of different shapes were obtained in stem extract being used as reducing and capping agents *C.iria* (L) stem extract formed approximately tubular and cuboidal AgNPs, respectively. This may be due to availability of different quantity and nature of capping agents present in the stem extract. This is also supported by the shifts of the peaks obtained in the FTIR analysis. EDX spectra recorded from the silver nanoparticles were shown in Figure 5 (right). From EDX spectra, it is clear that silver nanoparticles reduced by *C.iria* (L) stem extract have the weight percentage of silver as 78.12%.

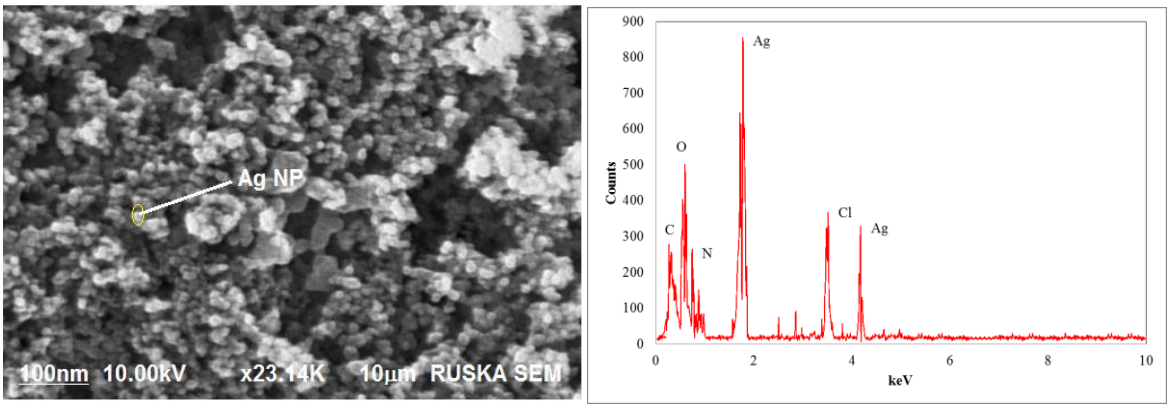

Figure 5: SEM micrograph of agents *C.iria* (L) stem extract-silver nanoparticles (left) and corresponding EDX spectra (right)

3.5 TEM Studies

The size distribution of nanoparticles in general is an important issue as nanoparticles exhibit different physical and chemical properties depending on their shape and size. Transmission electron microscopy (TEM) is therefore one of the most adapted techniques to study the size and shape of the nanoparticles and provide their distribution. It is important to note that the majority of the TEM studies were performed on plant extracted green synthesis of silver nanoparticles. The use of medicinal plants in the synthesis of Ag NPs is not only used for size and shape control but also used to provide properties to the Ag NPs along with the antimicrobial properties of the plant. The TEM images provide monodispersed nanoparticles in each case, indicating that the polyphenols act not only as a reducing agent but also as a capping agent and therefore restrict their growth to 60 nm (Figure 6).

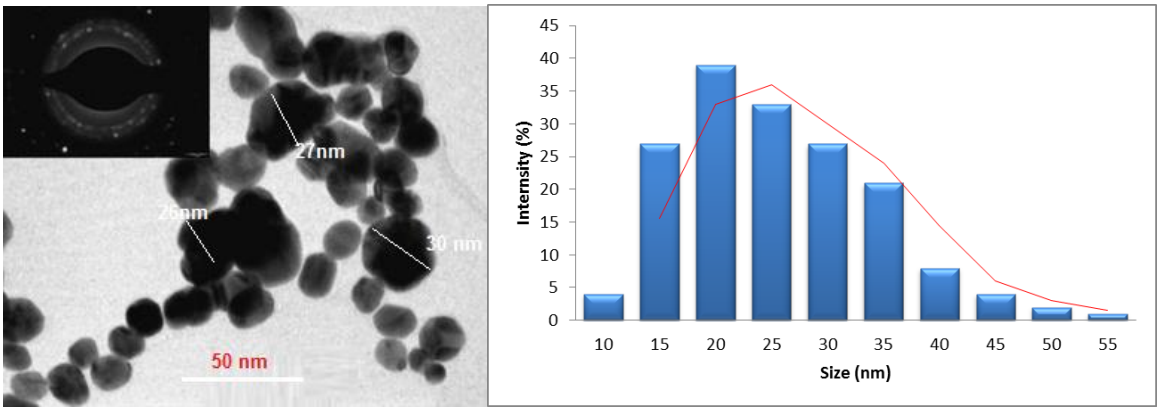

Figure 6: TEM image of silver nanoparticles synthesized using *C.iria* L stem and particles size distribution (right) inset SAED pattern

The TEM images of the particles thus obtained show spherical particles with a wide size distribution with 75% of the nanoparticles presenting particle size between 10 and 35 nm (Figure 6). Less than 10% of the nanoparticles were under 10 nm in size and between 40 to 55 nm. Most of the particles in the TEM image are polydispersed, nevertheless spherically shaped. Crystalline structure was confirmed by SAED pattern (inset picture). SAED pattern shows that green synthesized silver nanoparticles are of crystalline nature and few of them were recorded in the form of aggregates. The four diffraction ring (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) lattice planes could be indexed on the basis of the face-centered cubic (fcc) structure for silver. SAED shows five diffraction rings of fcc for silver. SAED report clearly indicates that synthesized silver nanoparticles are of crystalline structure.

4 Conclusion

During the last decades, many efforts were put into the development of new green synthesis methods. This present study stated the green-mediated synthesis of silver nanoparticles using the extract of easily available *C.iria* weed. The broad peak was observed at 447 nm for silver nanoparticles. Thus, the synthesized nanoparticles showed cubical and spherical-structured nanoparticles with agglomeration which was characterized by SEM and TEM. Purity and component of silver nanoparticles were confirmed by EDX.

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