Synthesis of silver nanoparticle using
*D. carota* extract

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Abstract

Biosynthesis of silver nanoparticles (NPs) using *D. carota* extract was investigated for various concentrations of *D. carota* extract. The aqueous silver ions were reduced into silver NPs when they interacted with *D. carota* extract. The silver NPs were characterized by UV-visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. XRD measurements show that the average size of silver NPs was 20 nm. UV-visible spectra show that the surface plasmon resonance peak of silver is observed at 415 nm. FTIR measurements indicate the presence in *D. carota* extract of ascorbic acid which is responsible for reducing and capping bioreduced silver NPs. TEM measurement shows that most silver NPs are spherical in shape.

Keywords: silver nanoparticles, *D. carota*, UV-visible, Fourier transform infrared spectroscopy, x-ray diffraction

Classification numbers: 2.00, 2.03, 4.02, 5.00

1. Introduction

Application of green chemistry for the synthesis of biocompatible metal nanoparticles (NPs) has gained considerable attention in recent years for potential applications in biomedicine [1, 2]. Integration of green chemistry principles to nanotechnology is one of the key issues in nanoscience research. The development of the concept of green nanoparticle preparation has grown the need for environmentally benign metal nanoparticle synthesis protocols to avoid adverse effects in medical applications [3].

Metal NPs are being widely used nowadays in areas such as photography, catalysis, biosensing, imaging, drug delivery, photonics, optoelectronics, biological labelling, nanodevice fabrication, surface enhanced Raman scattering (SERS) and in medicine [4–6] due to their unique electrical, optical as well as biological properties such as high thermal conductivity, high resistance to oxidation and antibacterial activity. The size, shape and surface morphology play a vital role in controlling the physical, chemical, optical and electronic properties of nanomaterials. Silver NPs are of particular interest because of their unique properties such as good electrical conductivity, chemical stability, catalytic and antibacterial activity [7].

Metal NPs have been synthesized using sodium borohydride as reducing agent which is highly reactive and causes potential environmental and biological risks. Utilization of nontoxic chemicals, environmentally benign solvents and renewable materials are some of the key issues that merit important consideration in a green synthesis strategy [8, 9].

The *D. carota* (carrot) gets its characteristic and bright orange colour from *β*-carotene, which is metabolized into vitamin A in humans when bile salts are present in the intestines. Massive overconsumption of *D. carota* can cause carotenosis, a benign condition in which the skin turns orange. *D. carota* are also rich in dietary fibre, antioxidants and minerals. Lack of vitamin A can cause poor vision, including night vision, and vision can be restored by adding it back into the diet. Ethnomedically, the roots are used to treat digestive problems, intestinal parasites and tonsillitis or constipation.

Green synthesis of silver NPs using citrus limon [7], latex of jatropha curcas [10], starch [11], banana peel extract [12], leaf extract of rosa rugosa [13], seed extract of jatropha curcas [14], sucrose and maltose [15], hibiscus rosa sinensis [16], cohlospernum gossypium [17] and honey [18] have been reported.

In the present work, a simple and green synthesis of Ag NPs using *D. carota* extract has been performed. The *D. carota* extract was used as a bioreductant for the synthesis of silver NPs.
2. Experimental

2.1. Material and methods
Silver nitrate is obtained from Sigma-Aldrich chemicals. *D. carota* has been collected from a local supermarket in Kodaikanal, Tamil Nadu, India.

2.2. Preparation of *D. carota* extract
Fresh *D. carota* (carrot) was washed several times with de-ionized water. Then 170 g of *D. carota* was cut finely and crushed in a mixer grinder with 100 ml distilled water. The mixture was filtered to get the extract. The extract is used as reducing agent and stabilizer. Figure 1 shows the freshly prepared *D. carota* extract.

2.3. Preparation of silver nanoparticles
For the green synthesis of silver nanoparticles, 4 ml of *D. carota* extract was added to a vigorously stirred 30 ml aqueous solution of AgNO₃ (5 × 10⁻⁴ M) and stirring continued for 1 min at room temperature. The solution changed from light orange to dark red colour which indicates the formation of silver nanoparticle. This procedure was repeated for 5 ml of *D. carota* extract with 30 ml aqueous solution of AgNO₃ (5 × 10⁻⁴ M). It is found that reduction takes place rapidly with increasing addition of the extract. The absorption spectra of prepared silver nanoparticles were carried out in different days to find out the time variation (1st, 3rd, 6th, 9th and 12th day). The prepared silver NPs were dried at 200 °C. The dried powders were taken for the characterizations such as x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). Figure 2 shows the prepared solution of silver nanoparticles (a) on the first day (light orange) and (b) after 12 days (dark red).

2.4. Characterizations of the synthesized nanoparticles
Synthesis of Ag NPs by reducing silver ion solution with *D. carota* extract is easily observed by UV-visible spectroscopy. The absorption spectra at different *D. carota* extract quantities were measured using a Shimadzu spectrophotometer (UV1700) in 300–800 nm range. Time-dependent variations were also observed (1st, 3rd, 6th, 9th and 12th day). The synthesized nanocrystalline powder was identified by the powder XRD method using an ‘X’ Pert PRO PANalytical diffractometer, using nickel-filtered Cu-Kα radiation as source and operated at 40 kV and 30 mA. The sample was scanned in the 2θ ranging from 10 to 80° for 2 s in the step scan mode. The observed peak positions were compared with the standard ICDD data and Miller indices were assigned to the Bragg peaks. FTIR measurements were obtained on a Nexus 670 FTIR instrument with the sample as KBr pellets. HR-TEM measurements were made using a JEOL JEM 2100 high resolution transmission electron microscope. This microscope enables viewing of the lattice resolution of 0.14 nm and point-to-point resolution of 0.19 nm.

3. Results and discussion

3.1. UV-visible spectral studies
The unique optical properties of metal nanoparticles originate from the collective oscillations of conduction electrons, which, when excited by electromagnetic (EM) radiation, are termed surface plasmon resonances (SPR). The factors that collectively lead to these oscillations are: (i) acceleration of the conduction electrons by the electric field of incident radiation, (ii) presence of restoring forces that result from the induced polarization in both the particle and surrounding medium and (iii) confinement of the electrons to dimensions smaller than the wavelength of light. The electric field of the incident EM radiation displaces the particle’s electrons from equilibrium and, in turn, produces a restoring force that results in oscillatory motion of the electrons with a characteristic frequency, that is, the SPR frequency. At the same time, the oscillating electrons induce polarization of the opposite direction in the surrounding medium, and this polarization reduces the restoring force for the electrons, thereby shifting the SPR to a lower frequency.

UV-visible absorption spectra have been proved to be quite sensitive to the formation of silver colloids because silver nanoparticles exhibit an intense absorption peak due to the surface plasmon (it describes the collective excitation of conduction electrons in a metal) excitation [19]. The absorption spectrum of isolated spherical particles is characterized by the Mie resonance occurring at a frequency \( \omega_o \) such that: \( \varepsilon_s(\omega_o) = -2\varepsilon_m \), where \( \varepsilon_s(\omega_o) \) is the dielectric function of the silver spherical particles and \( \varepsilon_m \) is the dielectric function of the surrounding medium [20].

When the frequency of the electromagnetic field becomes resonant with the coherent electron motion,
shows that the concentration of D. carota extract plays an important role in the formation of silver NPs, revealed by the intensity of SPR band around 420 nm increasing with increasing concentration of D. carota extract. The increase in absorbance could be influenced by an increase in amount of the absorbing species [27]. In the present case the increase in SPR band intensity can be correlated with an enhancement in the number of NPs in the reaction medium. The observed plasmon band is symmetric as the number of days increases, which indicates that the solution does not contain any aggregated particles.

The observed plasmon bands are broad with an absorption tail in the longer wavelengths, which could in principle be due to the size distribution of the particles [28]. In the case of 5 ml of D. carota extract, the FWHM value decreases as the number of days increases. But in the case of 4 ml of D. carota extract, the FWHM value decreases up to the 9th day and on the 12th day it becomes broader in width. The broad SPR bands observed at lower concentration of D. carota extract are due to large anisotropic particle. The broadness of peaks are also due to the inhomogeneous polarization of the particles in the electromagnetic field of the incoming light due to excitation of a different multiple mode which makes a peak in the spectrum at a different energy [29, 30]. At lower concentration of D. carota extract the ascorbic acid present in D. carota extract is insufficient to reduce silver ion and the SPR band is broad, indicating a particle of larger size. The narrow SPR band is characteristic of monodispersed spherical NPs. As the concentration of D. carota extract increases, more ascorbic acids are available to reduce silver ion and a large number of very small nanoparticles is formed giving rise to sharp and intense SPR [31, 32].

To monitor the stability of the silver colloid, we have measured the absorption spectra of the colloid after different periods of time. The reduction of silver NPs by D. carota extract has been monitored with rapid colour change of solution (see figure 2).

The stability of a colloidal solution can be influenced by the amount of the reducing agent and the absorbing species in a solution. The stability results from a potential barrier that develops as a result of the competition between weak the van der Waals forces of attraction and electrostatic repulsion. Metal sols normally aggregate through two mechanisms: cluster–particle aggregation and cluster–cluster aggregation. Aggregates are formed primarily by the addition of single
nanoparticles to a growing cluster in case of cluster–particle aggregation. In case of cluster–cluster aggregation, clusters of all sizes assimilate into larger clusters. An aggregating colloid can switch from one mechanism to the other as the number of particles becomes depleted [33]. In our case, we can assume that the silver nanoparticles possessed a negative charge due to the adsorbed ascorbate ions and thereby helped in preventing aggregation by electrostatic stabilization [34] while certain bio-organics present in the *D. carota* extract may also have brought about electrosteric stabilization.

### 3.2. XRD studies

The crystalline nature of Ag nanoparticle was confirmed from x-ray diffraction (XRD) analysis. Figure 4 shows the XRD pattern of the dried *D. carota* extract obtained from the colloid solution. No diffraction peak was observed in the 2θ range 20–80°. It shows that the dried *D. carota* extract is amorphous in nature.

The XRD pattern of the dried Ag nanoparticles synthesized using *D. carota* extract with various concentrations at various days is shown in figure 4. The four diffraction peaks were observed at 37.9°, 44.1°, 64.3° and 77.2° in the 2θ range 20–80° of sample 5 ml 12th day can be ascribed to the (111), (200), (220) and (311) reflection planes of face-centred cubic (fcc) structure of Ag phases. Two diffraction peaks observed at 37.8° and 43.9° in the 2θ range 20–80° of sample 5 ml 6th day can be ascribed to the (111) and (200) reflection planes of face-centred cubic (fcc) structure of Ag phases. Two diffraction peaks observed at 38° and 44.4° in the 2θ range 20–80° of sample 4 ml 12th day can be ascribed to the (111) and (200) reflection planes of face-centred cubic (fcc) structure of Ag phases. These diffraction peaks are well consistent with the standard data file JCPDS No 04–0783. As the concentration of *D. carota* extract increases the diffraction peaks corresponding to silver are increasing. The diffraction peaks also depend on time duration; as the number of days increases the diffraction peaks corresponding to silver are increasing. These observations indicate that the *D. carota* extract takes a longer time to reduce AgNO₃ into silver nanoparticles. In addition AgNO₃ needs more volume of *D. carota* extract to reduce into silver nanoparticles. These observations also confirm that the crystallization of bio-organic phase occurs on the surface of the Ag nanoparticles. The ratio between the intensity of the (200) and (111) diffraction peaks in the 5 ml 12th day sample is 0.42 which is lower than the conventional bulk intensity ratio 0.52, suggesting that the (111) plane has been predominantly oriented.

Generally, the broadening of peaks in the XRD patterns of solids is attributed to particle size effect [35]. Broader peaks signify smaller particle size and reflect the effects of the experimental conditions on the nucleation and growth of the crystal nuclei [36]. From the XRD patterns of the 5 ml 12th day and 4 ml 12th day samples, it can be seen that as *D. carota* extract concentration increases the peaks become sharper. This indicates that the powders have large crystallite domain sizes as the concentration increases.

In addition, residual peaks were also observed at 28.1° and 40.47° in all three samples (5 ml 12th day, 5 ml 6th day and 4 ml 12th day). These peaks are due to ascorbic acid present in *D. carota* extract. These diffraction peaks are well consistent with the standard data file JCPDS No 22–1536.

The average crystallite size calculated using Scherrer equation with the width of the (111) peak is found to be 21 nm (5 ml 12th day) and 16 nm (4 ml 12th day). The lattice parameter works out to be $a = 4.0966\,\text{Å}$ (5 ml 12th day) and $a = 4.0912\,\text{Å}$ (4 ml 12th day) which are in very good agreement with the standard data file JCPDS No 04–0783.

![Figure 4. X-ray diffraction pattern of *D. carota* extract and silver nanoparticles prepared with 4 ml (a) and 5 ml (b) of *D. carota* extract in 30 ml aqueous solution of AgNO₃ at different days.](image-url)
3.3. FTIR spectral studies

The IR spectra provided information about the local molecular environment of the organic molecules on the surface of nanoparticle. In the present work FTIR spectral measurements were carried out to identify the potential biomolecules in D. carota extract which is responsible for reducing and capping the bioreduced silver nanoparticles. Figure 5 shows the FTIR spectra of the silver nanoparticles and dried D. carota extract powder. From the FTIR spectra it may be inferred that vitamin C (ascorbic acid) was the probable capping agent on the nanoparticles.

Figure 5 shows interesting peaks at 1634, 1415, 1016 and 522 cm$^{-1}$ for dried D. carota extract. These peaks are assigned to C=C ring stretching, CH$_2$ scissoring, lactone ring deformation and OH out-of-plane deformation mode of vitamin C (ascorbic acid), respectively [37]. The OH stretching and CH stretching of vitamin C are also responsible for the peaks observed at 3417 and 2925 cm$^{-1}$, respectively. The C=C ring stretching and OH out of plane deformation mode of vitamin C are downshifted in prepared silver nanoparticles (5 ml 12th day and 5 ml 6th day). The more prominent vibrational mode observed at 1380 cm$^{-1}$ in silver nanoparticles may be due to CN stretching mode (N from silver nitrate). This indicates that the ascorbic acid present in D. carota extract is responsible for reduction of silver nanoparticles.

3.4. Transmission electron microscopy

Transmission electron microscopy (TEM) has been employed to characterize the size, shape and morphologies of formed Ag nanoparticles. Figure 6 shows the TEM image of the silver NPs (5 ml 12th day). It shows that most of the prepared silver NPs are spherical in shape.

4. Conclusion

The synthesis of silver nanoparticle using D. carota extract has been studied. It has produced silver nanostructures through efficient green nanochemistry methodology, avoiding the presence of hazardous and toxic solvents and waste. The prepared silver nanoparticles were characterized by UV-visible, FTIR and XRD techniques to identify the size of silver NPs and biomolecules acting as reducing agents. XRD measurements show that the average size of the prepared silver nanoparticle was 20 nm. Spherical shape of the prepared silver nanoparticles was determined from TEM image. FTIR measurement shows that ascorbic acid is present in D. carota extract. It also indicates that ascorbic acid present in D. carota extract is used as reducing agent.

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