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GREEN SYNTHESIS AND CHARACTERIZATION OF CURCUMA LONGA DERIVED SILVER NANOPARTICLES

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ABSTRACT

A simple, rapid, onsite and green biological strategy for the fabrication of silver nanoparticles (AgNPs) using Curcuma longa aqueous root extract has been reported in the current study. Curcuma longa aqueous root extract was used as reducing agent and protecting source which led to the formation of silver nanoparticles. Various reaction parameters were optimized in order to achieve monodispersed spherical silver nanoparticles having a large surface to volume ratio. Optimization of the concentration of precursor salt, the volume of Curcuma longa aqueous extract, temperature and pH effect was carried out to obtain small dimensional stable biosynthesized silver nanoparticles. As prepared Curcuma-AgNPs were chacterized by various techniques such as Fourier transform infrared (FTIR) Spectroscopy Ultra Violet-Visible (UV-Vis) spectroscopy, Transmission Electron Microscopy (TEM), X-ray Diffractometry (XRD) and Atomic Force Microscopy (AFM). These techniques showed that fabricated Curcuma-AgNPs were highly dispersed, spherical and crystalline in nature. TEM analysis indicated that most of the nanoparticles were spherical having an average size of 30.3±2nm.

Keywords: Green biological strategy, Curcuma longa, Silver nanoparticles, Aqueous extrac

INTRODUCTION

Study of dimensional nanomaterial is one of the emerging and fascinating areas of modern sciences which can contribute a huge role in modern technologies. Synthesis of metallic nanoparticles provided unique and novel properties due to controlling their dimensions at nanometric scale as compared to their bulk counter parts. Metal nanoparticles have been applied in various fields such as optical devices [1], photonics [2], biolabelling [3], biomedical [4], electrochemical analysis [5], biosensing [6], catalysis [7], information storage [8] and sensors [9]. Several synthetic strategies have been reported in literature such as, solvothermal [10], sonochemical [11], photochemical reduction [12], microwave-assisted [13], electrochemical [14], continuous-flow procedures [15], chemical reduction [16], physico-chemical [17], phytosynthesis [18] and thermal decomposition [19]. These conventional synthesis protocols of metal nanoparticles attribute in contamination of environment due to toxic solvents and chemicals.

In this regards, on the other hand, bio-synthetic procedures of metal nanoparticles have been considered as green ones due to avoiding the toxic materials. Currently, the attention of scientists diverted towards bio-fabrication of metal nanoparticles due to no toxicity and environmental friendly. Various plant extracts have been used as reducing and protecting agents for fabrication of silver nanoparticles such as, Canellas asiatica, Cinnamon zeylanicum bark, Artocarpus heterophyllus, Syzygium cumini, Curcuma longa tuber, Annona squamosa peel extract, Hibiscus rosa sinensis and some other extracts while replacing toxic solvents and reducing agents in form of proteins, sugars and flavonoid reducing materials [20-22].

In current study, we have synthesized silver nanoparticles (AgNPs) using Curcuma longa aqueous root extract. This procedure is a green and there was no use of any chemical or toxic solvent. Further fabricated nanoparticles were characterized by high-resolution techniques.

MATERIALS AND METHODS

1. Chemicals and Reagents

Various chemicals and reagents of high purity have been used during undertaken study. HCl (37%) and NaOH (98%) were achieved from Macron Fine Chemicals. 97% pure $AgNO_3$ have been purchased from Sigma-Aldrich and used directly in the study. All standards and solutions were prepared in deionized water and experiments were conducted at room temperature.

2. Fabrication and Characterization of curcuma longa root extract protected AgNPs

In synthetic protocol, curcuma longa root extract powder was prepared by grinding a suitable quantity using mortar and piston. 10 g of curcuma longa root powder has been dissolved in 1000 ml deionized water and kept the solution for 24 hrs. The solution was filtered and the extract has been used for fabrication of curcuma longa capped silver nanoparticles. In one step green synthesis of silver nanoparticles 1.0 ml of 0.1 M $AgNO_3$ was taken in a beaker containing 6.0 ml deionized water and put it into magnetic stirring for 2.0 min. then put 4.0ml of curcuma longa root extract at vigorous stirring for 10.0 min. The solution was put for some time to achieve stable silver nanoparticles.

Various instrumental advanced techniques have been used to characterize the biologically synthesized silver nanoparticles. An optimization study was carried out to optimize several reaction parameters using UV-vis spectrophotometer model U-3900. In order to study the interaction of curcuma longa root extract with fabricated silver nanoparticles, FTIR spectrophotometer of Bruker model vertex-70 has been used. Crystalline nature of extract protected AgNPs was performed by XRD model JES-FA/300 using Cu Kα (λ = 1.54060) radiation at 40 kV and provided 2°/min scanning rate. Solid sample was collected by drying the solution in a water bath. Surface roughness was determined using atomic force microscopy (AFM) model NT-MDT in intermittent contact having a force constant 40 N/m and frequency 300 kHz. . Morphological characterization of curcuma longa protected silver nanoparticles was carried out using Transmission electron microscopy of Gatan model JEOL JEM–2100 (UHR) at 300kV.

RESULTS AND DISCUSSION

1. Synthesis and Characterization

The colorimetric response of metallic nanoparticles play a key role and mostly it can be used to control the size and shape of nanoparticles. Various modes of Surface Plasmon Resonance (SPR) of metal nanoparticles reside within the colorimetric region of the spectrum. So, UV-vis spectroscopy is a preliminary tool for detection of metallic nanoparticles as well as optimization study. So, optimization of various reaction parameters is important in this regards. During this study, UV-vis spectroscopic analysis was carried out to optimize various reaction parameters. For this purpose initially, the optimization of the concentration of precursor salt ($AgNO_3$) was carried out and on the basis of blue shifted band in UV-vis spectroscopy 1.0 ml of 0.1 M $AgNO_3$ was optimized for further study as depicted in Fig.1 (a). Insight photograph also indicated that the colour was dark and increasing concentration affects the colour of nanoparticles. Experimental results as provided in Fig.1 (a) elaborated that by increasing the concentration of silver nitrate (1.0-5.0 ml of 0.1 M). This optimization study indicated that by increasing the concentration of $AgNO_3$ the concentration of silver ions increases and peak became broadened. The solution colour also becomes darker as shown inside the photograph. The broadened peak also indicated the increased agglomeration rate due to the free availability of excess Ag (I) ions in solution.

The optimization of the volume of extract was also conducted and results showed that 4.0 ml volume of extract gives good results hence it has been selected for further study as shown in Fig.1(b). pH has been considered an important factor during fabrication of nanoparticles, so we have optimized pH factor in order to achieve monodispersed spherical nanoparticles. On the basis of peak shifting, pH-7.45 has been selected during the study as shown in Fig.1(c). In an inside photograph colour change during the study also has been shown. It explained that with the increase in pH the colour become darker and nanoparticles become aggregated as indicated in spectral profile of pH in Fig. 1 (c). This Figure also indicated that in acidic pH range there was no peak of silver nanoparticles due to the addition of acid. In acidic media, the nanoparticles have been oxidized. Similarly, temperature effect was also studied and we selected normal room temperature in order to fabricate small size nanoparticles as shown in Fig.1 (d). Stirring rate optimization was also conducted and results have been shown in Fig. 1 (e). This Fig indicated that no prominent affect was found by increasing the stirring rate. On the basis of small difference, 200 rpm was optimized in the formation of AgNPs. Inside photograph also indicates that there was no change in colour observed by increasing the stirring rate.

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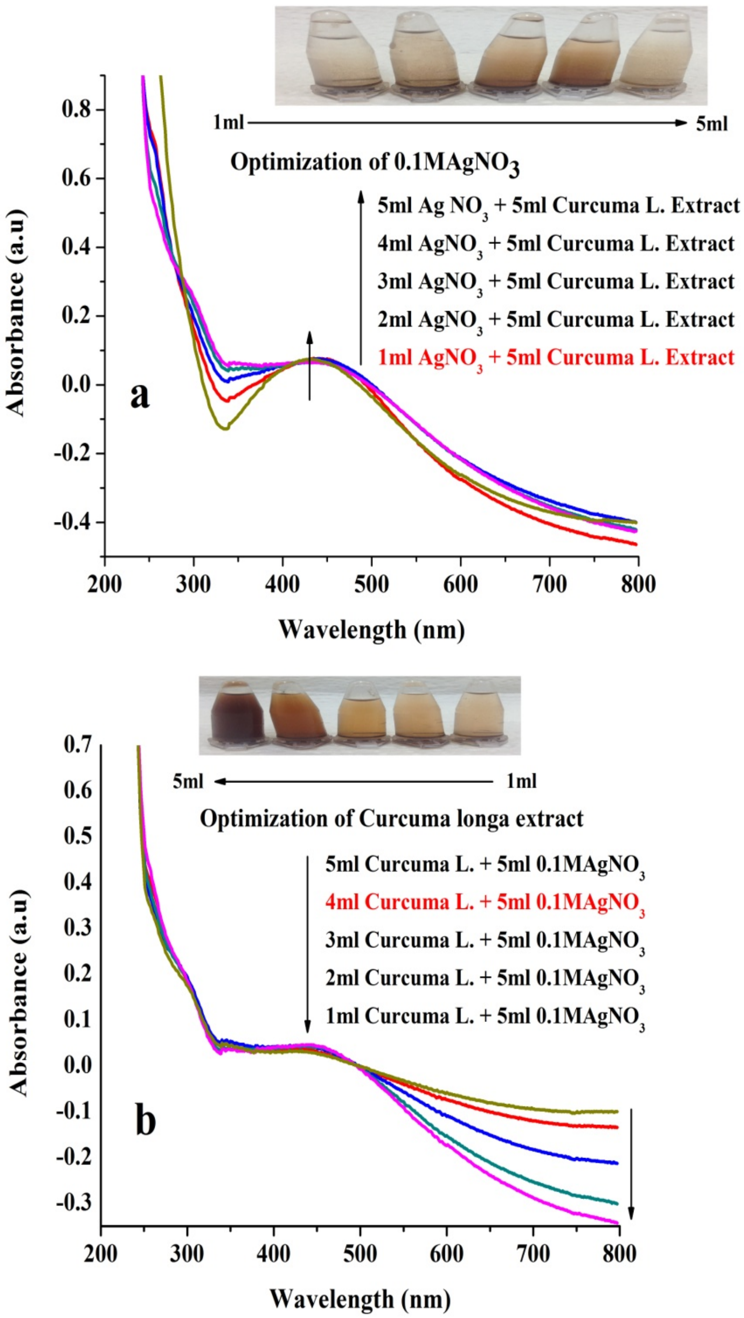
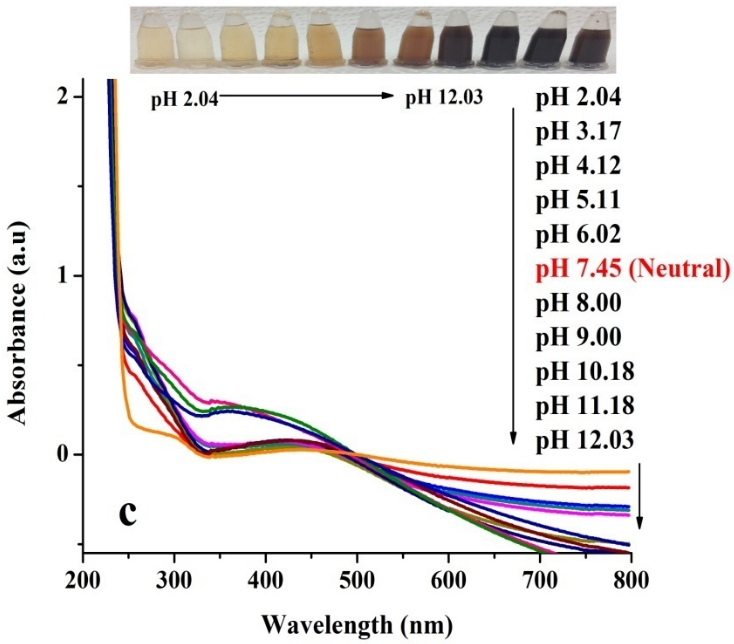


1ml
5ml
Optimization of 0.1MAgNO3
5ml Ag NO3 + 5ml Curcuma L. Extract
4ml AgNO3 + 5ml Curcuma L. Extract
3ml AgNO3 + 5ml Curcuma L. Extract
2ml AgNO3 + 5ml Curcuma L. Extract
1ml AgNO3 + 5ml Curcuma L. Extract
Absorbance (a.u)
a
Wavelength (nm)
5ml
1ml
Optimization of Curcuma longa extract
5ml Curcuma L. + 5ml 0.1MAgNO3
4ml Curcuma L. + 5ml 0.1MAgNO3
3ml Curcuma L. + 5ml 0.1MAgNO3
2ml Curcuma L. + 5ml 0.1MAgNO3
1ml Curcuma L. + 5ml 0.1MAgNO3
Absorbance (a.u)
b
Wavelength (nm)


pH 2.04
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pH 10.18
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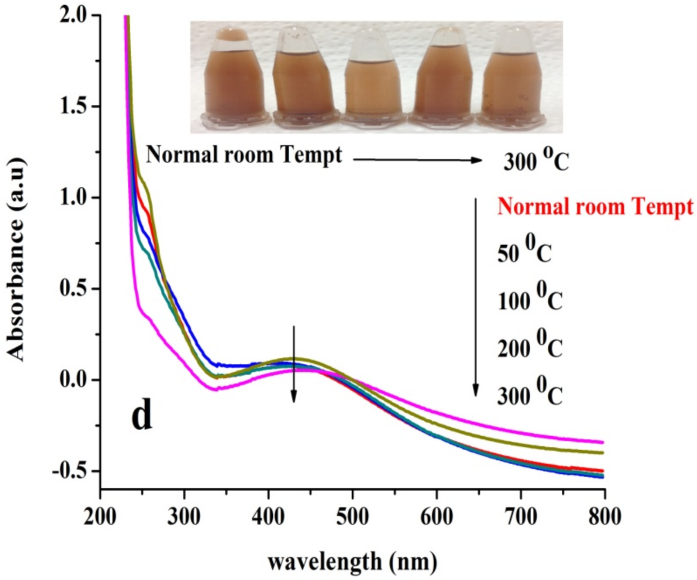
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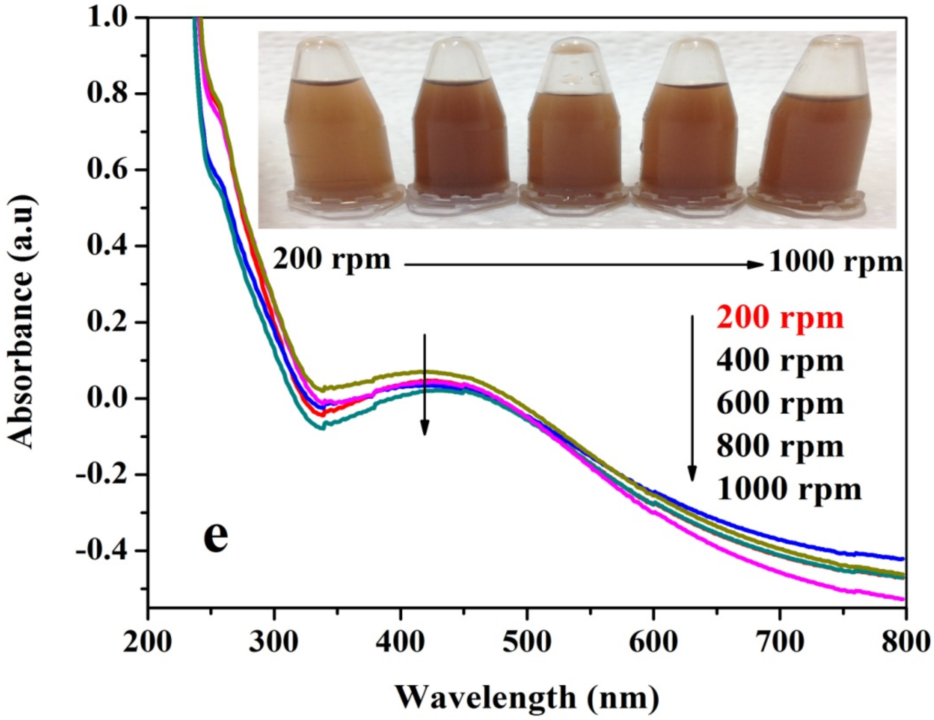

Fig.1. Optimization of 0.1M $AgNO_3$ (a), volume of curcuma longa root extract (b), effect of pH (c), Temperature study (d) and effect of stirring on the formation of curcuma longa protected silver nanoparticles (e).

Optimization studies indicated the small size monodispersed silver nanoparticles. In order to study the interactions between the AgNPs and curcuma longa extract, FT-IR study was conducted as depicted in Fig. 2. FT-IR spectrum of pure curcuma longa root extract and curcuma extract protected AgNPs has been shown in Fig. 2 (a) and (b) respectively. This Figure showed that after interaction of curcuma longa with AgNPs the peak at 3241 cm^{-1} slightly red shifted as well as the appearance of a new peak at 1623 cm^{-1} indicated the interaction of curcuma with AgNPs. The appearance of a new sharp peak at 1391 cm^{-1} attributed the formation of curcuma protected silver nanoparticles. Similarly, appearance of some new peaks and disappearance of several peaks in the spectrum of AgNPs in (b) clearly indicated the interaction of AgNPs with the curcuma root extract.

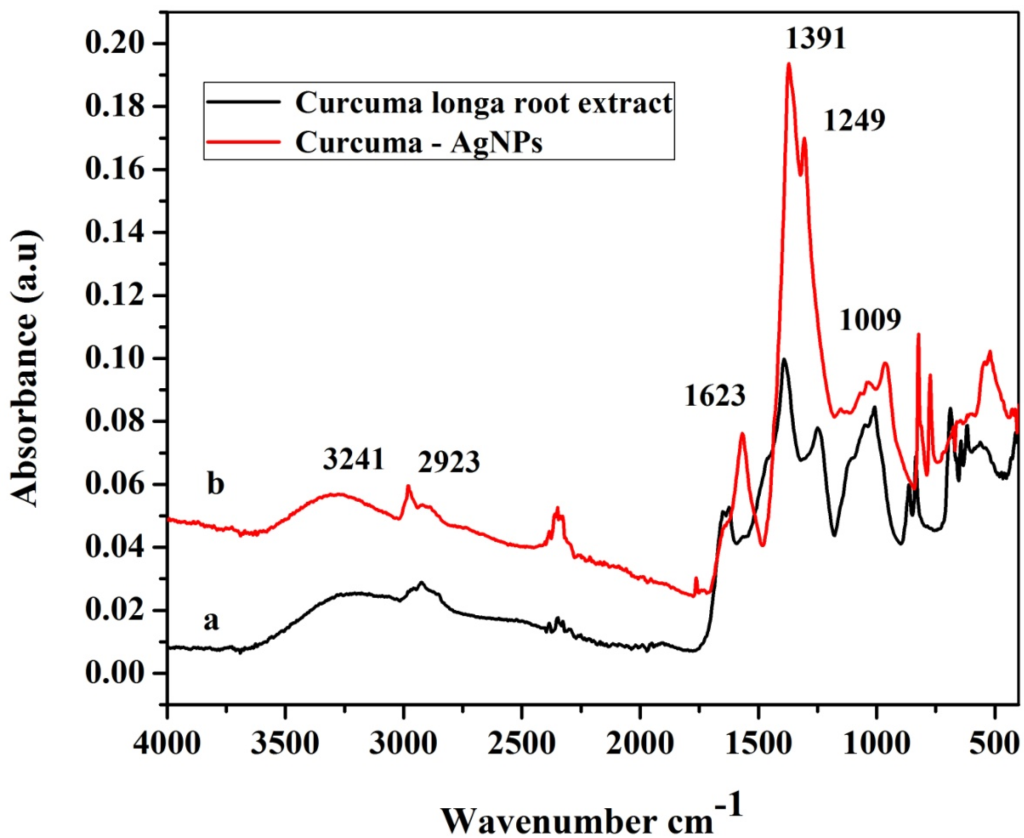

Fig.2. FT-IR spectra of a pure curcuma longa root extract (a) and curcuma longa root extract capped AgNPs.

The crystalline nature of fabricated silver nanoparticles was characterized using XRD. Obtained result has been shown in Fig. 3. the result indicated the crystalline nature of silver nanoparticles having 2Θ values of 38°, 44°, 63°, and 78° representing Bragg's peaks with (111), (200), (220) and (311) planes respectively as indicated in Fig. 3. Although there have been found some other peaks due to glass and extract.

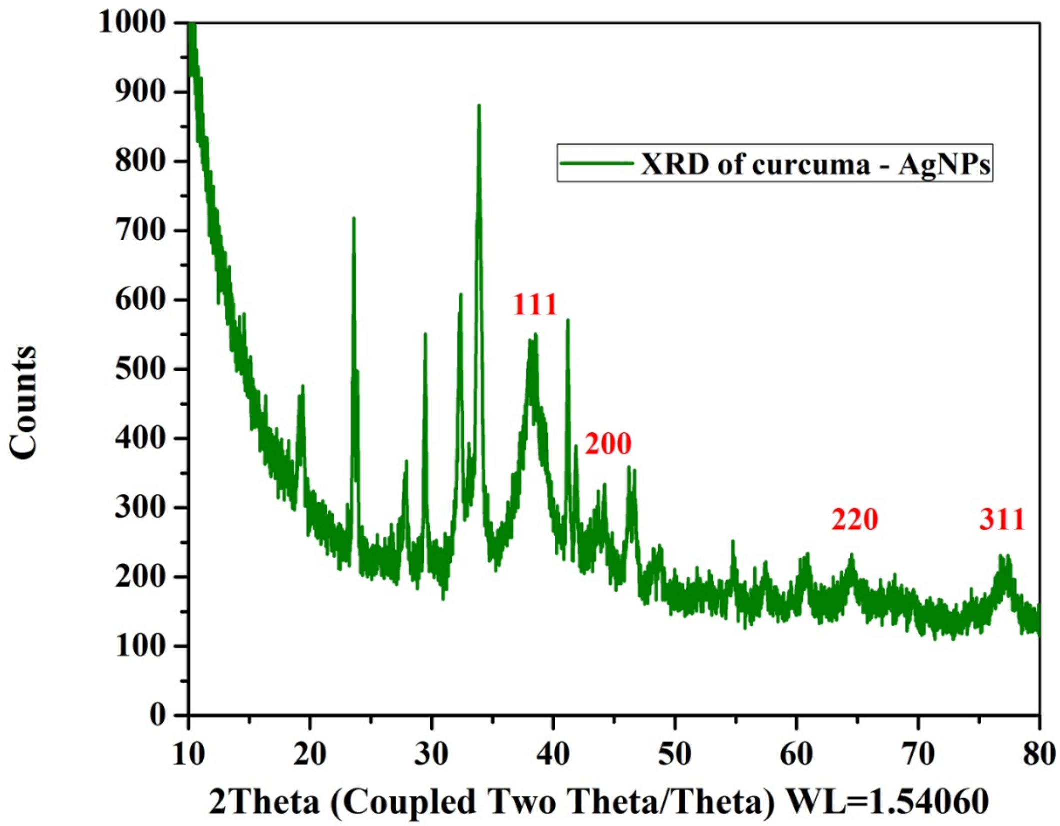

Fig.3. XRD pattern of Curcuma longa root extract protected silver nanoparticles.

In order to study the surface roughness AFM study was conducted and results of pure curcuma Fig.4 (a) and curcuma-AgNPs (b) indicated that there was no surface roughness found in case of pure extract while after the formation of AgNPs the surface roughness increases hence the biologically synthesized AgNPs have an excellent sensing, antimicrobial and catalytic activity.

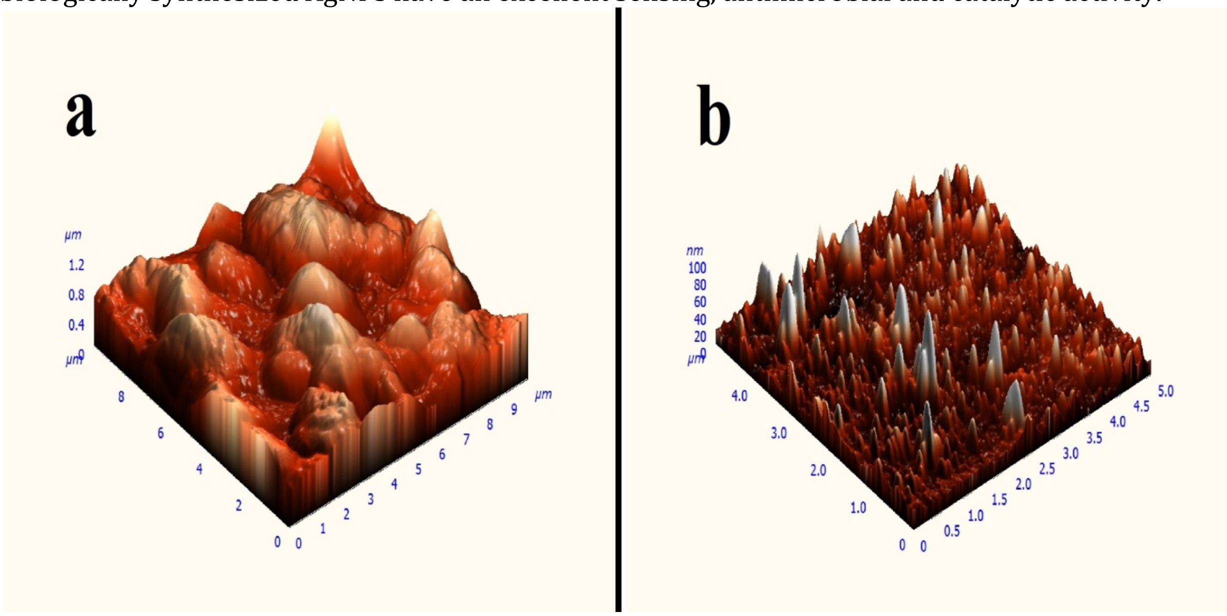

Fig. 4. Three-dimensional images of pure curcuma longa extract (a), and curcuma-AgNPs (b).

The morphological study was conducted using TEM instrument and results indicated that the extract protects the silver nanoparticles. The average size of nanoparticles was found to be 30.3±2nm as depicted in Fig. 5 (a) and (b). The Fig. 5 further elaborated that the AgNPs protected strongly by curcuma longa root extract.

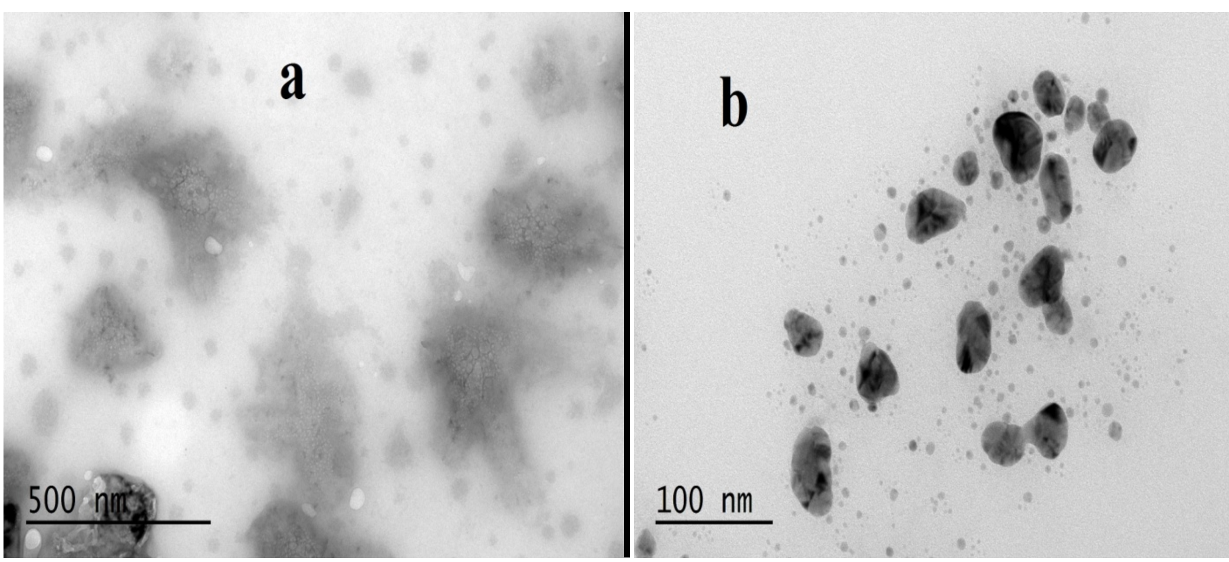

Fig.5. TEM images of a pure curcuma longa root extract (a) and curcuma longa root extract capped AgNPs.

The possible reaction mechanism for the formation of curcuma longa protected AgNPs has been shown in two reactions as under. Curcuma longa as an aldehyde can reduce silver ions to Ag-NPs. The possible chemical equations for preparing the Ag-NPs are:

$Ag^{+}_{(aq)}$ + Curcuma Longa $\xrightarrow{\text{Stirring}}$ [Ag (Curcuma Longa)]$^{+}$………… (1)

[Ag (Curcuma Longa)]$^{+}$ + R-CHO $\xrightarrow{\text{24hrs}}$ [Ag (Curcuma Longa)] + R-COOH …… (2)

After dispersion of silver ions in the C. longa aqueous solution matrix (Equation 1), the extract was reacted with the Ag^{+} (aq) to form [Ag (Curcuma longa)]$^{+}$ complex, which reacted with aldehyde groups in the molecular structure of the methanolic extract to form [Ag (Curcuma longa)], due to the reduction of silver ions through the oxidation of aldehyde to carboxylic acid groups (Equation 2).

CONCLUSIONS

Green and an economical synthetic route was developed first time for large scale production of stable curcuma longa root extract protected AgNPs using curcuma longa as protecting/ reducing agent. The investigated synthetic route is simpler, economical, environmentally friendly, easy and green as well as highly effective. Further, we characterized the fabricated silver nanoparticles by highly advanced characterization techniques. Results indicated that the fabricated silver nanoparticles were small in size and highly stable. On the basis of these results, we suggested that these nanoparticles can be used efficiently as catalytic, antibacterial and sensing of toxic species.

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