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Biosynthesis, characterization and antioxidant activity of *Solanum nigrum*-mediated Ag and Cu nanoparticles

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Abstract

The development in nanoscience has introduced the use of plant parts for the biosynthesis of metal nanoparticles which offers an alternate to the chemical synthesis. Silver and copper nanoparticles (NPs) are found biologically active so has great importance against infectious microbes. In this paper a green and one pot method was developed for the synthesis of silver and copper nanoparticles from leaf extract of *Solanumnigrum* plant. The prepared AgNPs and CuNPs were characterized by FTIR, UV–Vis, and XRD. UV–vis spectra of AgNPs displayed maxima absorption peak at 460 nm while CuNPs displayed peak at 400 nm. XRD analysis revealed that AgNPs and CuNPs have crystalline structure with average size 42.7 nm and 27.8 nm respectively. Moreover the synthesized CuNPs showed showed strong antioxidant activity than AgNPs nanoparticles.

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Introduction

Nanotechnology is the technique which deals the matter at nanoscale. Nanoscience may be used towards the other disciplines such as materials science, chemistry, physics, biology and engineering. It is a fast-developing field of science and is playing an important role for the welfare of mankind (Xi-Feng Zhang *et al.*, 2016; Tamilvanan *et al.*, 2014). Owing to their unique properties Ag NPs have a number of uses such as anti-cancer, larvicidal, catalytic, antifungal, anti-inflammatory, antiviral, antibacterial, anti-angiogenic and wound healing etc. Silver nanoparticles have been utilized broadly in the in food storage, health care industry, and house-hold utensils (Xi-Feng Zhang *et al.*, 2016;JannathulFirdhouse and Lalitha, 2015).Cu nanoparticles have applications in optical, imaging, magnetic, catalytic, electrical and biomedical (Tamilvanan *et al*, 2014; Manoj *et al*,2016). The phytosynthetic approach is advantageous over physical, chemical, and microbial approaches due simplicity of process, no need of hazardous chemicals, eco-friendly and cost effective (ArumugamSengottaiyan *et al.*, 2016), The plant extract plays an significant role in determining the characteristics of the nanoparticles due to the presence of different concentrations and combinations of organic reducing agents. A typical recipe is the one pot synthesis which consists of mixing the aqueous extract of the plant with relevant metal salt solution (Ravindra Kale *et al*, 2018). *Solanumnigrum* Linn. Belongs to family Solanaceae. All the parts of this plant is used in medicine. It has great importance in Ayurveda. It has distinct purple-black berries and white flower (Mason Muller 2015). The biomolecules like flavonoids, saponinstannins, alkaloids, and proteins are the main constituents in *solanumnigrum (*PronobGogoi and Islam, 2012).

Solanumnigrum have mainly alkaloids, glycosides, steroids, flavonoids, protein, carbohydrates, and amino acids. These phytochemical constituents used for cure of numerous diseases. So it can be used in the pharmaceutical and cosmetic productions (Rashmi Pandey and Rashmi Arnold, 2017). It is frequently used to cure inflammatory conditions, liver disorders, painful periods, chronic skin ailments (psoriasis and ringworm), fevers, eye diseases, hydrophobia, diarrhoea, etc. It contains the constituents, such as total alkaloid, steroidal saponins, steroid alkaloid, and glycoprotein, showing anti-tumour activity (Mohamed Saleem. *et al.*, 2010).

In the present study extract of leaves of *Solanumnigrum* plant was used for preparation of Ag NPs and Cu NPs. Synthesized nanoparticles were characterized by means of different techniques and their antioxidant activity was also evaluated.

Materials and methods

Collection of the plant and Preparation of the plant extract

The plant's leaves were obtained in the month of May, 2018 from the village ChamroopurChak#62, Lahore (Pakistan) and taken to the lab. The plant leaves were washed with running water andwere dried for 5 days in the shade. Then these leaves were powdered by means mortar. Aqueous extract of the leaves was prepared from leaves powder (5g) in 300 ml distilled water by boiling mixture for 20 min. Then the extract was clarified via Whatman filter paper.

Preparation of salt solution

Silver nitrate (0.01 M) solution and Copper sulphate (0.1 M) solution was made by adding $AgNO_3$ and$CuSO_4$ saltrespectively in double distill water.

Preparation of Ag and Cu nanoparticles

The plant extract (10 ml) was mixed to the relevant salt solution (50 ml) in flasks and these flasks were placed on the shaker for 5 h at 60 °C. The colour of the mixed solution was changed gradually from light colourto dark colour, which specify the creation of NPs.

Separation and purification of preparedAg and Cu nanoparticles

The manufactured silver and copper NPs were separated and cleaned by means of centrifugation at 5000 rpm for 20 min. The obtained pellets were washed usingthe solution ethanol and water (1:2) then again centrifugedat 5000 rpm for 20 min. Theprocess was repeated for thrice to eliminate all the unreacted plant biomass. Then the obtained pellets were dried at 250˚C for 1 hrs.

Characterization of nanoparticles

The nanoparticles were characterized via Uv. Visi. FTIR and X-Ray diffraction methods. UV-Visible analysis: Change in color of the mixed solution was observed and the production of nanoparticles was monitored via periodically recording the spectrum on the UV-vis. spectrophotometer BMS (Biotechnology Medical Services), Single beam, Quartz Cells, UN-2600.

Fourier Transform Infra-red analysis: The FTIR-analysis was done to investigate the plant biomolecules which are liable for the creation of nanoparticles by Midac MC 2000 Spectrometer.

X-Ray diffraction analysis: The dried sample of the prepared NPs was analyzed by X-Ray diffraction on a XRD machine [XRD-D8 Discover, Bruker, Germany], Cu Kα radiation (λ = 0.15406 nm) with increment 0.10.

Antioxidant activity of Ag and Cu nanoparticles

Antioxidant Activity of Ag NPs and Cu NPs synthesized with the leaf extract of *solanumnigrum* was estimated by DPPH (2, 2-diphenyl-1-picryl-hydrazyl) method. The solution of DPPH (0.1mM) was made in 95% methyl alcohol and this prepared solution (1ml) was mixed to the 3.0 ml of produced NPs solution (10-60 ug/ml). Then each reaction mixture was kept at 40ºC for 35 min in the dark condition. After 35 min the colour of the reaction mixture waschanged and its reduction in absorbance was checked at 517 nm by UV-Vis.study. Ascorbic acid was taken as a standard.

DPPH scavenging action of the prepared nanoparticles was calculated as follow

% Inhibition = A0 – A1\ A0 *100

Here

A0= UV-Vis. absorbance without NPs (control)

A1= UV-Vis. absorbance with NPs.

Results

Preparation of silver and copper nanoparticles

Silver and copper NPs were manufactured by mixing the extract of *solanumnigrum* leaves with the relevant metal salt solution.

Table 1. XRD data for Size calculation of Ag NPs.

θ value (degree)	d- pacing (Å)	FWHM (degree)	Intensity (CPS)	Particle size (nm)
31.521	2.8491	0.368	110	23.44
40.500	2.2260	0.184	70	48.11
44.229	2.0421	0.241	45	37.23
56.18	1.6360	0.169	30	55.70

Colour change of the mixed solution was detected after 5 hrs.from greenish yellow to dark brown for Ag and yellowish green to brownish green (fig. 2) which is the indication of the creation of Ag and Cu nanoparticles respectively.

Characterization of Ag and Cu nanoparticles

Uv visible analysis of Ag andCu nanoparticles : UV-Vis. spectra of Ag and Cu NPs manufactured by plant extract displayed maximum absorbance at 460nm and 400 nm respectively (fig. 3) due to Surface Plasmon resonance and gradually enhancethe intensity with the passage of time.

FTIR analysis of Ag and Cu nanoparticles: For the investigation of biomolecules which are liable for the creation of metal nanoparticles FT-IR analysis of the manufactured nanoparticles was done and the spectra are given here. FTIR spectrum of Ag nanoparticles (fig. 4) displayed peak in the range of 3570–3200 cm^{-1} which matches to hydroxyl O–H while peak at 3560–3200 cm^{-1} resembles to H-bonded OH stretching and peak at 3400–3370 and 3345–3320 cm^{-1} matches to N–H primary amine and NH stretching respectively, while Carboxylate group at1573 cm^{-1} and thepeak at 1392 cm^{-1} is corresponding to C–H bending of Methyl, at 1095 cm^{-1} matches to (Si–O–C) Organic siloxane, Thiol or thioether and at 663 cm^{-1} matchesto CH_2–S– (C–S stretch).

Table 2. XRD data for Size calculation of Cu-nanoparticles.

θ value (degree)	d- pacing (Å)	FWHM (degree)	Intensity (CPS)	Particle size (nm)
28.326	3.1469	0.366	110	23.40
31.577	2.8295	0.355	115	24.31
40.537	2.2256	0.270	105	32.79
45.429	1.9945	0.293	50	30.73

Table 3. Antioxidant Activity of Ag and Cu nanoparticles.

Nanoparticle (NPs)	Absorbance of control (nm)	Absorbance of sample (nm)	DPPH Antioxidant activity (%)
Silver (Ag)	0.046	0.039	13.33 %
Copper (Cu)	0.22	0.024	89.09%

Copper nanoparticles showed peak in the range of 3570–3200 cm^{-1} agrees to H-bonded of OH stretch and to O–H hydroxyl group, while peak at 3400–3380 cm^{-1} matches to N–H of primary amine, NH stretch, at 2360-2314 cm^{-1} characterize nitriles group andat 15989cm^{-1} to stretching of Carbonyl group, at 1408 cm^{-1} to Methyl bending of C–H , at 1315 cm^{-1}suggest Carboxylate whilepeak at 667 cm^{-1} belongs to Thioldue to CH_2–S– (C–S stretch).

Fig. 1. Photograph of *Solanumnigrum* (Solanaceae).

X-Ray Diffraction analysis of Ag and Cu nanoparticles: The XRD image of Ag and Cu NPs, manufactured by the extract of *Solanumnigrum* leaf was presented here.

The XRD image of Ag NPs (fig. 5) displayed five prominent peaks of 2θ value in the range of 10°to 70°. Mean calculated size of the produced particles was 42.7 nm with size collection 23.44 to 55.70 nm as shown in Table 1.

XRD image of Cu-nanoparticles (fig. 6) displayed four clear peaks of 2θ value in the range of 10 °to 70°. The average calculated size of the manufactured particles was 27.8 nm with size collection 23.40 to 32.79 nm as shown in Table 2.

Antioxidant activity of Ag and Cu nanoparticles

The antioxidant activity of the produced Ag NPs and Cu NPs was evaluated by means of DPPH method.

The purple colour of DPPH solution (fig. 7) goes yellow till colourless (fig. 8) on adding the nanoparticles which specifies the existence of antioxidant activity.

Discussion

Silver and copper nanoparticles were prepared by mixing the *S. nigrum* leaf extract with the solution of the silver nitrate and copper sulphate.

Fig. 2. Silver (left) and copper (right) nanoparticles mixture after incubation.

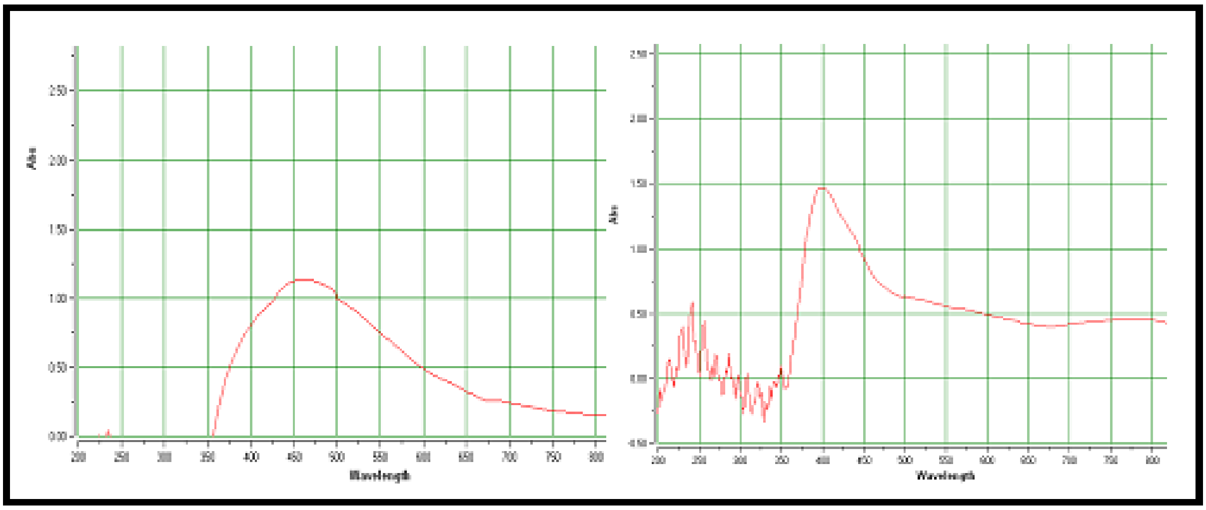

Fig. 3. UV Vis. Graph of Silver (left) and copper (right) nanoparticles after incubation.

The alteration in colour in the reaction mixture was detected after mixing from yellow to dark brown (fig. 2 left) for Ag nanoparticles which is in agreement with literature (Johnson and Joy Prabu, 2015; ArumugamSengottaiyan *et al*., 2016) and yellowish green to brownish (fig. 2 right) green for copper nanoparticles which is similar with (Usha *et al*., 2017; PanduRaju *et al*., 2016), and the indication of the creation of Ag and Cu nanoparticles respectively. UV–Vis study is an important method to establish the creation and stability of metal NPs.

The UV–Vis spectrum of Ag NPs manufactured by leaf extract of *S.nigrum*presented a prominent peak at 460 nm (fig. 3 left) which suggest the occurrence of AgNPs (Noura El-Ahmady El-Naggar *et al*., 2018; AlirezaEbrahiminezhad *et al*., 2016).

Brause *et al*. (2002) reported that Uv Visible spectrum of Metal NPs are primarily subjected to SPR. The peak ofUv Visible is associated with particle size.

Here the UvVis.spectrum of manufactured copper NPs by leaf extract of *S. nigrum* displayed a prominent peak at 400 nm (fig. 3 right) which suggest the existence of CuNPs(Usha*et al*., 2017; PanduRaju*et al*., 2016).

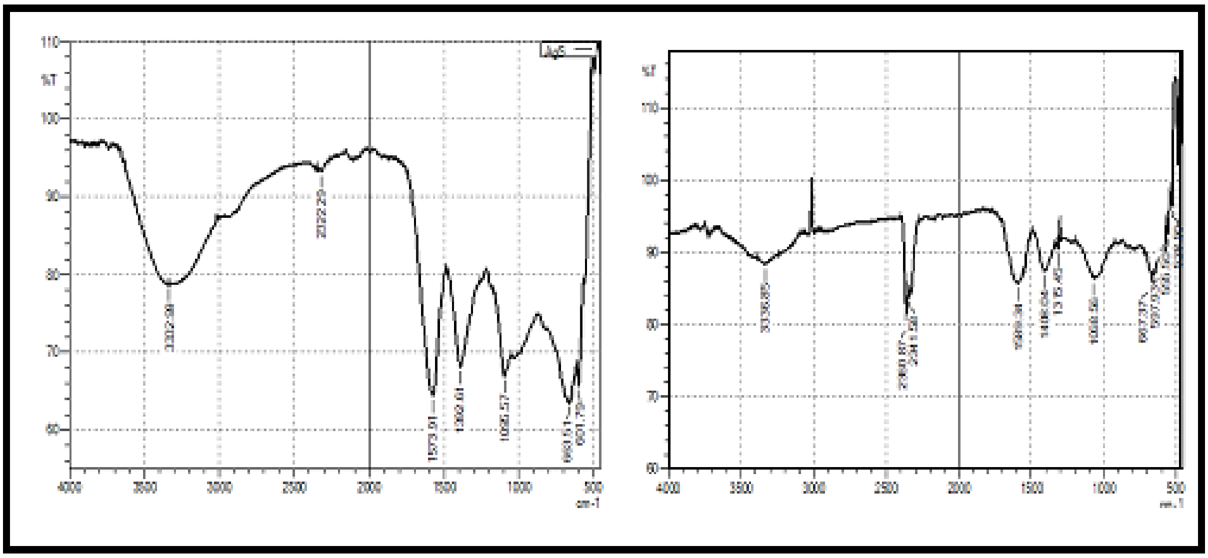

Fig. 4. FTIR spectrum of silver (left) and copper (right) nanoparticles.

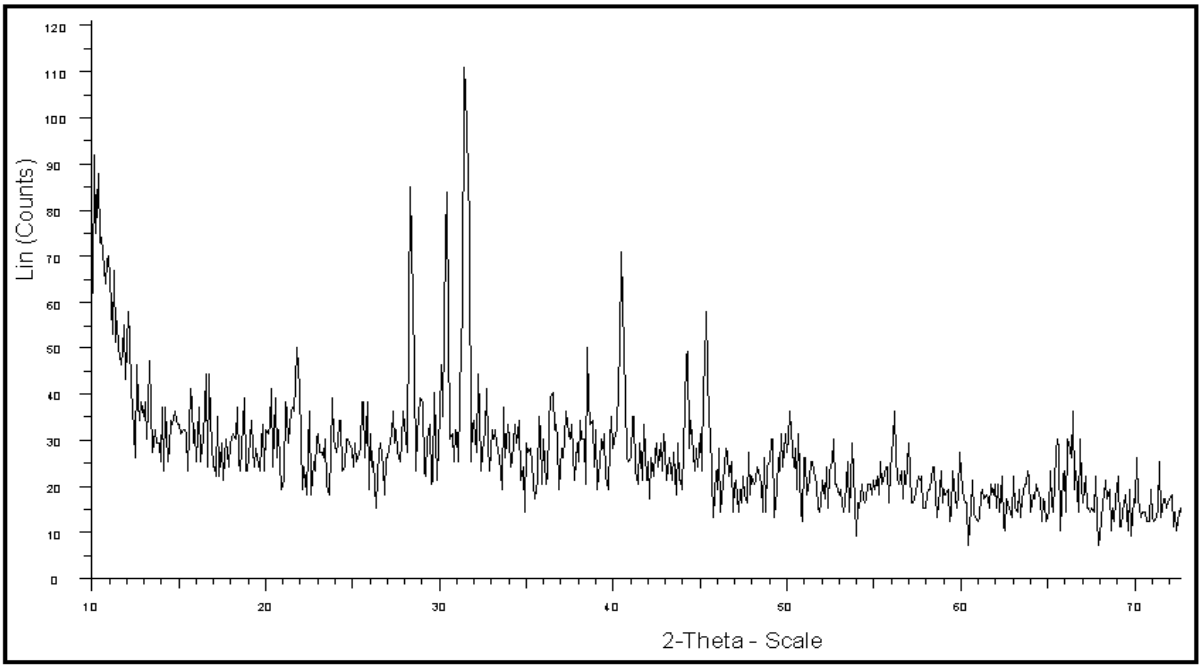

Fig. 5. XRD image of Ag- nanoparticles.

FTIR analysis (fig. 4) play a key role for the investigation of surface chemistry of so numerous plant metabolites, comprising alkaloids,terpenoids, phenolic acids, polyphenols, carbohydrates and proteins, showed key role in the generation of nanoparticles(Rama Koyyati *et al.*, 2016; AlirezaEbrahiminezhad *et al.*, 2016).Silver nanoparticles created by *Solanumnigrum* leaf presented four prominent diffraction peaks of 2θ value at 2θ= 31.521, 40.500, 44.229 and 56.180(fig. 5) which revealed the crystalline nature of Ag nanoparticles with average size 42.7 nm(table 1), similar results were reported in litrature (ManikandanVelu *et al.*, 2017;Meenakshi , 2017; Paramasivam Premasudha *et al*, 2015).

The XRD design of Cu-nanoparticles (fig. 6) has also revealed five diffraction peaks at 2θ= 28.326, 31.577, 40.537, and 45.429 which exhibit the crystalline nature of Cu nanoparticles (Ravindra*et al*, 2011; Batoool and Masood, 2017). Mean size of the prepared copper nanoparticles was 27.8 nm (table 2).

Antioxidant action of the manufactured Silver(Ag) and Copper(Cu) nanoparticles was evaluated by DPPH method. The purple solution of DPPH changed yellow till colourless on adding of nanoparticles, which specifies the existence of antioxidant activity (Upendra Nagaich, *et al*, 2016).

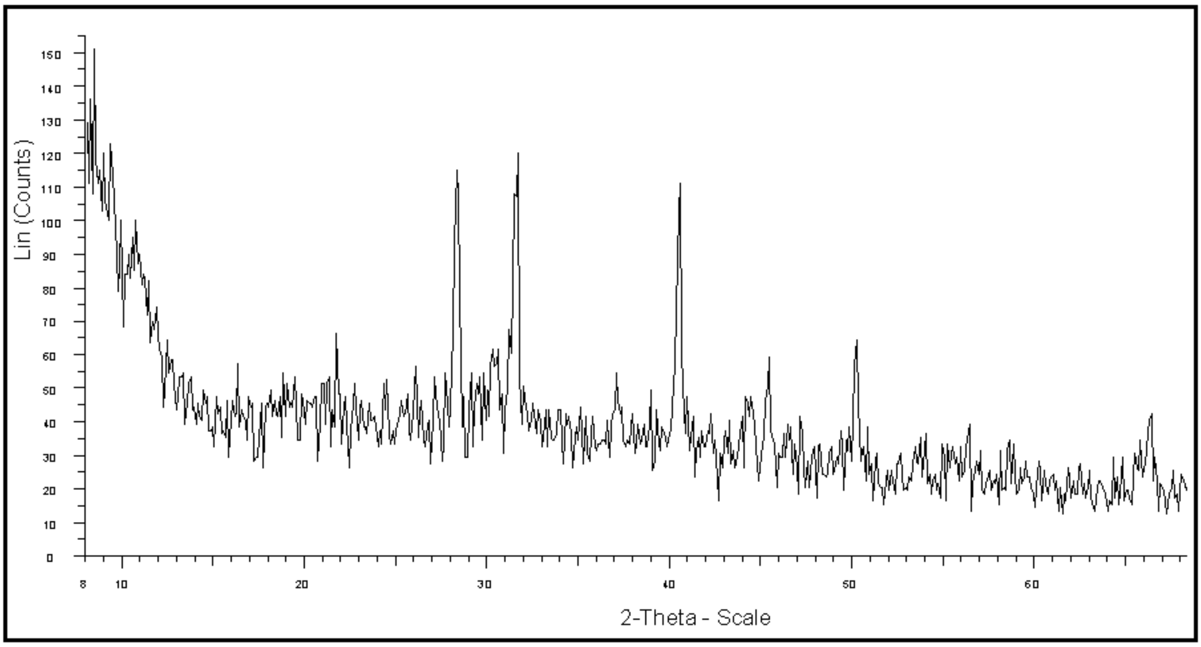

Fig. 6. XRD pattern of Cu- nanoparticles.

The antioxidants react with DPPH and convert it to 1, 1-diphenyl-2-picryl hydrazine with decolorisation. So, the manufactured Ag and Cu nanoparticles have considerable antioxidant activity due to the existence of biomolecules on the upper surface of nanoparticles (Palaniselvam Kuppusamy *et al.*, 2016).

Fig. 7. DPPH solution show purple colour before the addition of metal nanoparticles.

Fig. 8. Change in colour of DPPH solution after the addition of metal nanoparticles.

Moreover, the prepared copper nanoparticles showed higher antioxidant activity than silver nanoparticles (Ghosh *et al.*, 2015;Manjul Gondwal and Geeta Joshi nee Pant, 2018). So both of these nanoparticles can be used as efficient tools for applications in biomedical.

Conclusion

Production of metal nanoparticles using plant extract is widely studied in the last two decades due to ecofriendly behavior of plant metabolites. Here we have presented a very easy and eco-friendly process for the production of silver and copper nanoparticles which showed efficient antioxidant activity.

So these plant mediated Ag and Cu nanoparticles can be used in various fields such as therapeutics, pharmaceuticals, sustainable and renewable energy, catalytic and in other commercial products.

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