ejpmr, 2017,4(2), 676-679

SJIF Impact Factor 4.161

EUROPEAN JOURNAL OF PHARMACEUTICAL AND MEDICAL RESEARCH

www.ejpmr.com

Research Article

ISSN 2394-3211

EJPMR

UV VISIBLE SPECTROSCOPIC ANALYSIS OF GREEN SYNTHESIZED SILVER NANO PARTICLES

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Article Received on 20/12/2016 **Article Revised on 09/01/2016** **Article Accepted on 31/01/2017**

ABSTRACT

Green synthesis of AgNPs was carried out using *Cardiospermum halicacabum* leaves extract. Here plant extract plays dual role in biosynthesis as reducing as well as stabilizing agent. The mechanism of the reaction involves the reduction of aqueous metal ion in the presence of plant extract. The formation of AgNPs was confirmed by the visible colour change from colourless to brownish yellow colour with the addition of plant extract to silver nitrate solution. Further, it was quantitatively monitored by UV-Visible spectroscopic studies. It can be clearly seen that after 5 min, there was a change in the surface plasmon resonance (SPR) absorption of wavelength in the range of 400-500 nm. It can also be observed that, the intensity of the peak was gradually increases with increasing $AgNO_3$ concentration, indicating the reduction of Ag^+ to Ag^0. This is due to the formation of AgNPs with the progress of the reaction because the intensity of the SPR is directly proportional to the density of the nanoparticles presented in that solution. It showed a distinct SPR band around 430 nm, indicating the formation of the AgNPs. The formation of AgNPs was confirmed by the UV Visible spectra. The dispersions of silver nanoparticles display intense colours due to the plasmon resonance absorption. The surface of a metal is like plasma, having free electrons in the conduction band and positively charged nuclei. Surface plasmon resonance (SPR) is a collective excitation of the electrons in the conduction band; near the surface of the nanoparticles. Electrons are limited to specific vibrations modes by the particle's size and shape. Therefore, metallic nanoparticles have characteristic optical absorption spectrums in the UV-Visible region.

KEYWORDS: Silver nanoparticles, UV-Vis, SPR, SEM.

INTRODUCTION

In metal nanoparticles such as in silver, the conduction band and valence band lie very close to each other in which electrons move freely. These free electrons give rise to a SPR absorption band,[1-4] occurring due to the collective oscillation of electrons of silver nano particles in resonance with the light wave.[5] Classically, a polarization of the electrons with respect to much heavier ionic core of silver spherical nanoparticles is induced from an incoming wave of electric field.[3] This results in a restoring force creating a dipolar oscillation of all the electrons in same phase. The resonance between the frequency of the electromagnetic field and coherent electron motion results in a strong absorption which is the origin of the observed colour. Here the colour of the prepared silver nanoparticles is light yellow to brown having different shades. This absorption strongly depends on the particle size, dielectric medium and chemical surroundings.[2-3] Small spherical nano particles (<20 nm) exhibit a single surface Plasmon band.[6] UV-visible spectroscopy is one of the popular characterization techniques to determine particle formation and its properties. Furthermore, it is known that the spectrum surface plasmon resonance of nanoparticles is influenced by the size, shape, inter particle interactions, free electron density and surrounding medium,[7] which indicates that it is an efficient tool for monitoring the electron injection and aggregation of NPs. The aim of the present study is to synthesize colloidal silver nanoparticles using simple and economical method. We have used *Cardiospermum halicacabum* leaves extract to prepare silver nanoparticles. Also the effect of maturing time and concentration of $AgNO_3$ on size is studied using UV-Visible spectroscopy.

MATERIALS AND METHODS

Chemicals

AR grade silver nitrate ($AgNO_3$) purchased from Merck, India. All other chemicals and solvents used were of analytical grade available commercially.

Plant materials

The plant *Cardiospermum halicacabum* leaves were dried and extracted with ethanol using soxhlet apparatus for 24 hours. The ethanol extract is used for the determination of antimicrobial and antioxidant activity.

Preparation of plant extract, 1mM $AgNO_3$ and AgNPs

The fresh leaves extract of *Cardiospermum halicacabum* were weighed and dissolved in sterile distilled water (10mg/100ml). For the preparation of 1mM $AgNO_3$, 0.016gms of AgNO3 weighed accurately and made upto 100 ml using sterile distilled water. For the preparation of AgNPs, 90ml of various concentrations of silver nitrate solutions (2 mM; 1mM; 0.75mM and 0.5 mM) were added to each 10 ml of plant extract to make up a final solution 100 ml and centrifuged at 18,000 rpm for 25 min.

UV-Vis Spectra analysis

The reduction of pure Ag^+ ions was monitored by measuring the UV-Vis spectrum of the reaction medium at 5 hours after diluting a small aliquot of the sample into distilled water. UV-Vis spectral analysis was done by using UV-Vis spectrophotometer UV-1800 and Sl-210 Double Beam UV Visible Spectrophotometer (Elico).

SEM analysis of silver nano particles

Scanning electron microscopic (SEM) analysis was done using VEGA3 TESCAN machine, Japan. Thin films of the sample were prepared on a carbon coated copper grid by just dropping a very small amount of the sample on the grid. Extra solution was removed using a blotting paper and then the films on the SEM grid were allowed to dry by putting it under a mercury lamp for 5 min.

RESULTS AND DISCUSSION

Silver nanoparticles were readily synthesized with the plant extract without the use of any additional stabilizing agents. UV-Vis 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.[8] We observed the UV spectra of silver colloids of different concentrations in the range of 300 to 800 nm. Well defined plasmon bands around 430 nm (minimum at 430.5 nm to a maximum at 435 nm) were seen [**Fig.1 (a-d**]. The increase in maximum absorbance at different concentration is due to the particle density, which strongly depends on the amount of silver reduction at the surface of the medium [9-12]. Sols with a single visible extinction band near 400 nm are characteristic of silver particles substantially smaller than the wavelength of light.[13]

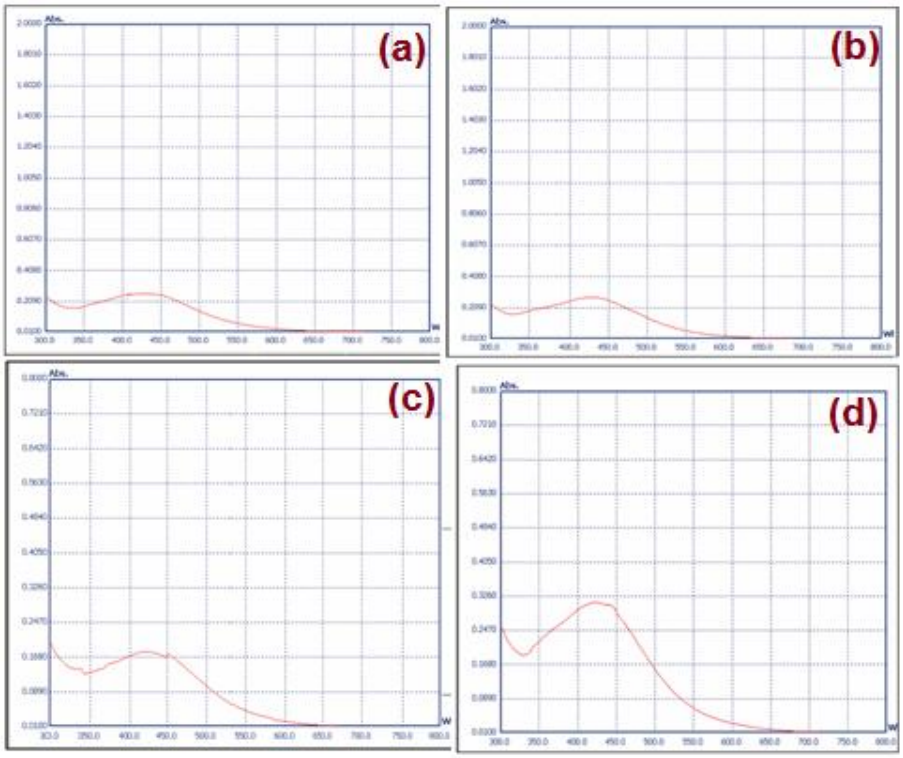

Fig.1. UV-Vis absorption spectra of synthezied silver nanoparticle solutions at different $AgNO_3$ concentrations. (a) 0.5 mM $AgNO_3$ concentration (b) 0.75 mM $AgNO_3$ concentration (c) 1 mM $AgNO_3$ concentration (d) 2 mM $AgNO_3$ concentration used.

It is known that the colour of metal particles is caused by the sum of the effects of absorption and scattering of visible light. According to Mie's theory, small spherical nanocrystals should exhibit a single surface plasmon

band, whereas anisotropic particles should exhibit two or three bands, depending on their shape. Absorption spectra of larger metal colloidal dispersions can exhibit broad or additional bands in the UV-Visible range due to the excitation of plasma resonances or quadrupole and higher multipole plasmon excitation.[6]

Effects of aggregation and stability of silver nano particles

To confirm the effect of aggregation and stability of silver nanoparticle solutions, we measured the absorption spectra of one of the colloid systems (1mM $AgNO_3$) at different time interval. As shown in **Fig. 2**, in the initial three-week period there is no obvious change in the peak position (Plasmon resonance peak at 430.5), except for slight increase in absorbance intensity. The stable position of the absorbance peak indicates that the particles do not aggregate. This spectra demonstrate that the silver nanoparticle colloidal solution can remain stable for about 3weeks.

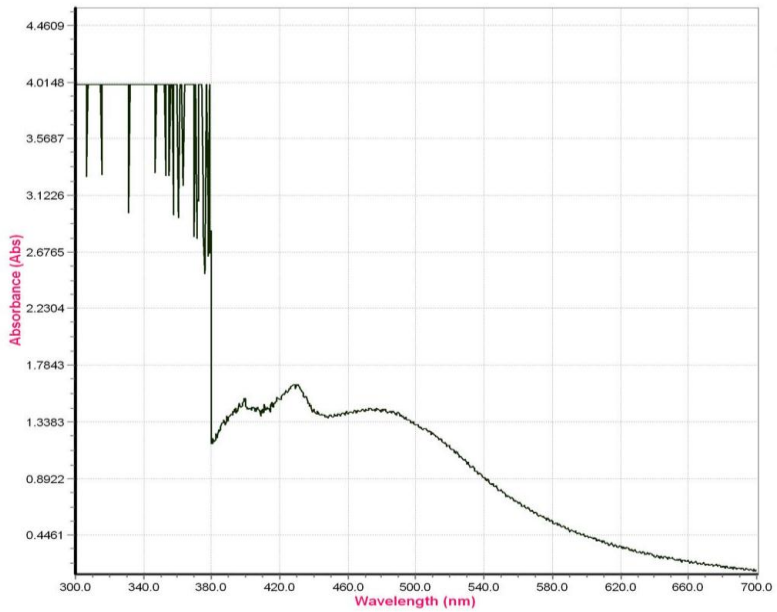

Fig.2. UV-Vis spectra of silver nanoparticle solution recorded after 3 weeks

Scattering from a sample is typically very sensitive to the aggregation state of the sample, with the scattering contribution increasing as the particles aggregate to a greater extent. For example, the optical properties of silver nanoparticles change when particles aggregate and the conduction electrons near each particle surface become delocalized and are shared amongst neighbouring particles. When this occurs, the surface plasmon resonance shifts to lower energies, causing the absorption and scattering peaks to red-shift to longer wavelengths. UV-Visible spectroscopy can be used as a simple and reliable method for monitoring the stability of nanoparticle solutions. As the particles destabilize, the original extinction peak will decrease in intensity (due to the depletion of stable nanoparticles), and often the peak will broaden or a secondary peak will form at longer wavelengths (due to the formation of aggregates). In Fig.2 secondary peak also formed at wave length of 480 nm.

Table: **1. Optical characteristics of synthesized nanoparticle solutions: Peak absorbance (nm)**

$AgNO_3$ concentration	Wave length (nm)	Absorbance (Abs)
0.5 mM	433	0.2140
0.75 mM	431	0.2170
1.0 mM	430.5	0.2190
2.0 mM	430	0.3180
1.0 mM (After 3 weeks)	430.5	1.6334

Scanning Electron Microscope

SEM observation of 1.0 mM $AgNO_3$ used phytosynthezied AgNPs showed in Fig.3. Scanning Electron Microscope analysis showed that the synthesized AgNPs are polydispersed (**Fig.3**), with particle size range from 70-100 nm.

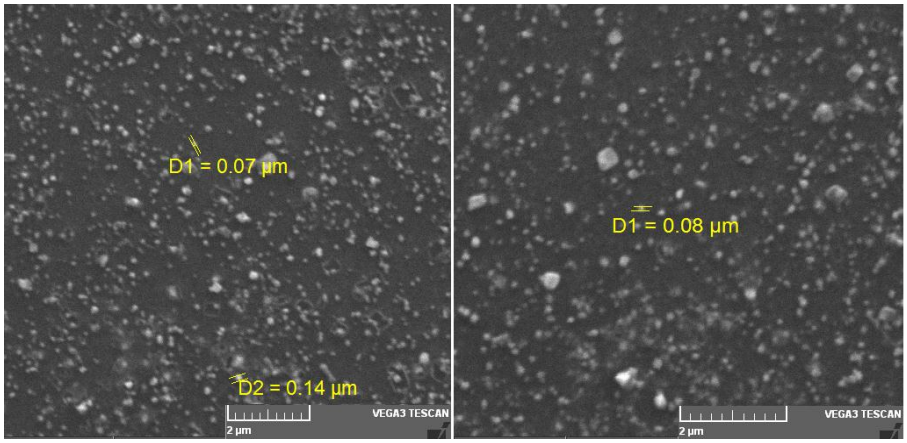

Fig.3. SEM images synthezied nano particles at different magnifications.

CONCLUSION

The silver nanoparticles obtained using green route has been characterized by UV-Vis spectra and SEM, the obtained silver nanoparticles are of sizes between 70 nm and 100 nm. It is observed that as the concentration of $AgNO_3$ increases the absorption band becomes sharper. The UV-Vis spectra of the different nanoparticles concentrations in our study show asymmetric absorption peak. When the system is polydisperse, the peak shape is asymmetric, These results mean that the size distribution becomes broader, and the colloid system is polydispersed. To confirm the stability of silver nanoparticle solutions, we measured the absorption spectra of one of the colloid systems at different time intervals. As shown in Figure 2, in the initial three-week period there is no obvious change in the peak position, except for slight increase in absorbance intensity. The stable position of the absorbance peak indicates that the particles do not aggregate. This spectra demonstrate that the silver nanoparticle colloidal solution can remain stable for about 3 weeks.

REFERENCES

1. Taleb A, Petit C, Pileni MP. Optical Properties of Self-Assembled 2D and 3D Superlattices of Silver Nanoparticles. J Phys Chem, 1998; B102: 2214-2220.
2. Noginov MA, Zhu G, Bahoura M, Adegoke J, Small C, Ritzo BA, Drachev VP, Shalaev VM. Enhancement of surface plasmons in an Ag aggregate by optical gain in a dielectric medium. Opt Lett., 2006; 31(20): 3022-3024.
3. Link S, El-Sayed MA. Optical properties and ultrafast dynamics of metallic nanocrystals. Annu Rev Phys Chem., 2003; 54: 331-366.
4. Kreibig U, Vollmer M. Optical Properties of Metal Clusters, Springer Series in Materials Science, 1995; 25: Berlin.
5. Nath SS, Chakdar D, Gope G. Preparation of Silver Nanoparticles and Their Characterization, Nanotrends—A Journal of Nanotechnology and Its Application, 2007: 02.
6. He R, Qian X, Yin Y, Zhu Z. Preparation of polychrome silver nanoparticles in different solvents. J Mater Chem., 2002; 12: 3783-3786.
7. Ghosh SK, Pal T. Interparticle coupling effect on the surface plasmon resonance of gold nanoparticles: from theory to applications. Chem Rev., 2007; 107(11): 4797-862.
8. Gao Z, Gao F, Shastri KK, Zhang B. Frequency-selective propagation of localized spoof surface Plasmon in a graded plasmonic resonator chain. Sci Rep., 2016; 6: 25576.
9. Panacek A, Kvitek L, Prucek R. Silver colloid nanoparticles: synthesis, characterization, and their antibacterial activity. J Phys Chem B., 2006; 110(33): 6248–16253.
10. Suchomel P, Kvitek L, Panacek A, Prucek R, Hrbac J, Vecerova R. Comparative Study of Antimicrobial Activity of AgBr and Ag Nanoparticles (NPs). PLoS ONE., 2015; 10(3): e0119202. doi:10.1371/journal.pone.0119202
11. Theobald JA, Oxtoby NS, Phillips MA, Champness NR, Benton PH. Controlling molecular deposition and layer structure with supramolecular surface assemblies. Nature, 2003; 424(6952): 1029-1031.
12. C. Luo,Y. Zhang,X. Zeng,Y. Zeng,Y. Wang. The role of poly (ethylene glycol) in the formation of silver nanoparticles. J Colloids Int Sci., 2005; 288(2): 444-448.
13. Creighton JA, Blatchford CG, Albrecht MG. Plasma resonance enhancement of Raman scattering by pyridine adsorbed on silver or gold sol particles of size comparable to the excitation wavelength. J Chem Soc Farad Trans 2, 1979; 75(0): 790–798.