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Characterization Study of Green Synthesized Silver Nanoparticles using Cinnamon Bark (Cinnamomum Cassia) Extract

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Abstract

Problem: Synthesis of metal Nanoparticles (NPs) via environment friendly method is not as prevalent as the chemical methods. The plants of Indian habitat must be explored as the strong reducing and stabilizing agent in the field of synthesis of metal nanoparticles. These plant extracts have the potential to synthesize nanoparticles at very low cost, minimum laboratory requirement and easily available physiochemical conditions. **Approach:** In the present study, Green synthesis of Silver Nanoparticles (AgNPs) using Cinnamon Bark (Cinnamomum cassia) extract has been done. Cinnamon Bark is a common ingredient of Indian spice family which contains Cinnamaldehyde which acts as a reducing agent. The synthesis procedure has been carried out in a very simple and lucid way. **Findings:** Cinnamon is a good reducing as well as capping agent. Also, temperature is playing an important role which has been analysed. The synthesized AgNPs have been examined in aqueous as well as powdered form, using variety of characterization tools. The powdered form show good morphology even after several days of synthesis. **Conclusion:** The Silver nanoparticles in aquous form, when kept under normal environmental conditions, show coagulation in aqueous form within couple of days. But the powdered form are quite stable.

Keywords: Green synthesis, Silver Nanoparticles, Cinnamon Bark, Reducing agent, Characterization.

I. Introduction

Nanoscience deals with the material having its atleast one dimension in nanometer range 1-100 nm (Varadan et al, 2008). These nanomaterials show extraordinary properties due to which they are considered as a revolutionary material in this modern era. Enhance Surface to Volume Ratio, Quantum Confinement effect, Enhanced Permeability and Retention effect, LSPR effects (Zayats et al.,2005) etc are some of the extraordinary properties, exhibit by materials at nanoscale. There are various ways of synthesizing nano particles. Out

of these, Green method is gaining attention in the field of nano material because it is eco friendly, one step – one pot method of synthesis. From ancient days Bhashmas (metal nano powders) to modern days upcoming nano robots; the nano based materials have been serving mankind since time immemorial. India is well cultured with the Ayurvedic values. The nano materials in the form of Bhashmas and Rashayans (Shilpa V. Rajan et al, 2023) were used by our ancestors for multipurpose. India is also well background with floral habitat having medicinal values. Green method is gaining attention in the field of nano material because it is eco-friendly, one step-one pot method of synthesis. There has been emphasis on the experiment done in a basic laboratorial setup, requiring simple tools and techniques.

In the present study, reduction of Silver Nitrate Salt ($AgNO_3$) to Silver Nanoparticles (AgNPs), using cinnamon bark has been studied. Cinnamon contains flavoinoid (Rao et al, 2014) mainly Cinnamaldehyde which has functional groups capable of reducing and stabilizing Silver nanoparticles. The study suggests that the cinnamon is not as much efficient as the other reported reducing agents like clove or tulsi, to synthesize Silver nanoparticles in less time and normal room temperature, when taken in standard 1:10 ratio of Cinnamon extract and Silver Nitrate solution. Increasing the temperature fastens the process. The various characterizations of the synthesized NPs (both in aqueous and powder form) give a conclusive result.

II. Materials And Methods

Materials

1. Silver Nitrate ($AgNO_3$) 99% assay, molecular weight 169.87 gram (Research Lab company Catalogue No. 01333) has been bought from local chemical shop.
2. Cinnamon Bark (Cinnamon cassia) as shown in Figure No. 1 about 20 gram has been bought from local grocery shop from Ara Bihar.
3. Double Distilled water (DDW) has been used as aqueous medium and Ethanol (95% pure) has been used as cleaning and washing agent.
4. Whatman's No. 1 Filter paper Cytiva company Cat No. 1001-125 (Figure No. 2) has been used for micron level filteration.
5. Basic experimental instruments like Hot plate magnetic stirrer, Centrifugal machine (max 15000 rpm), digital pH meter, digital thermometer, digital milligram weighing machine, etc. are used.
6. All the experiments have been done at three different temperatures i.e. room temperature 28° C – 32° C, and 70° C and in dust free and direct sunlight restricted environment.

Fig 1 : Cinnamon Bark

Fig 2 : Whatman's No. 1 Filter Paper

Method

All the laboratorial flasks have been well treated with DDW and Ethanol, to avoid any dust.

Preparation of Cinnamon Extract

20 gram of Cinnamon is washed with DDW and Ethanol one by one and dried at room temperature. After 2 hours, it is grinded with mortar and pestle. The stuff is mixed with 250 ml of DDW and boiled for 10 min. The solution is left for cool down and filtered through Whatman's filter paper twice to obtain 150 ml of the extract.

It is here noted that cinnamon has been taken in higher quantity to get a higher concentration.

Preparation of Silver Nitrate Solution

3 mM concentrated Silver Nitrate solution is prepared by dissolving 500 mg of $AgNO_3$ (Molecular mass – 169.87 gram) in 1000 ml of DDW. The solution is kept at room temperature.

Green Synthesis

1000 ml of $AgNO_3$ (aq) is mixed with 100 ml of cinnamon extract solution (10:1). The mixture is divided into two parts each of 500 ml to examine them at two different temperature of 30° C and 70° C named as sample A and B respectively.

III. Result And Discussion

Characterization study in aqueous form

1) Color Change – Since, Nano sized metal particles exhibit Localised Surface Plasmon Resonance (LSPR), when they are explored to light. This phenonmenon occurs in Visible-IR regions for noble metals like Silver. It causes color change, which can be attributed to the formation of metal nanoparticles.

   In the present experiment, there is no color change even after 15 Hrs for the sample A kept at 30° C (Figure No. 3). However, when the sample A is left for 48 Hrs, it starts changing color from yellow to light brown, with precipitate formation in the solution (Figure No. 4). It means that the reduction process is slow and the particles have aggregated to form lumps. In the case of sample B, being heated at 70° C, it is showing color change (Figure No. 5) from yellow to deep brown takes place, only after 5 min, evidencing the occurrence of LSPR very fast. It may be said that the reduction process occurs easily and fast at higher temperature in the case of cinnamon bark extract as reducing agent, taken in 1/10 fraction.

Fig 3 : 30°C , 0 & 15 Hr.

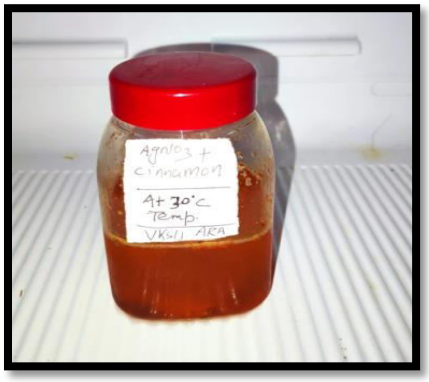

Fig 4: 30°C, 48 Hrs

Fig 5: 70°C, 5 Min

2) Ultraviolet Visible Spectroscopy – The two samples (A & B) have been done UV-Vis spectroscopic analysis after about 12 Hrs. The samples taken in cuvette are diluted to have absorbance intensity range 0 to 1. Sample A (Room temperature synthesis) is showing no any significant absorption peak (Figure No. 6), indicating that there is very little reduction of silver NPs. Sample B (At 60° C) is showing absorption peak at 465 nm with absorbance intensity 0.55 (Figure No. 7).

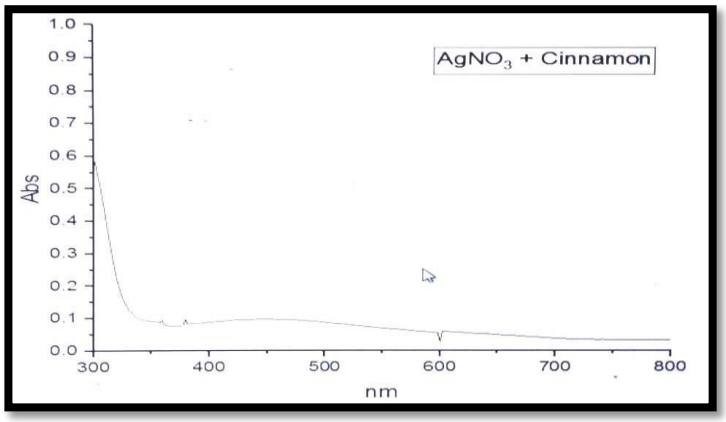

Fig 6 : UV Analysis Sample A (at room temp)

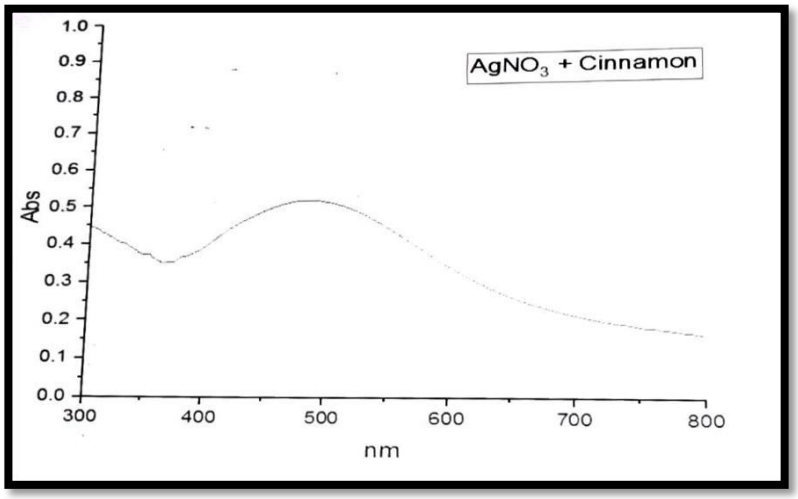

Fig 7 : UV Vis analysis Sample B (Synthesized at 70o C)

3) Fourier's Transform Infrared Spectroscopy (FTIR) – FTIR detects the functional groups responsible for the reduction process. Figure 8 shows the FTIR peak at different wave number (1/λ). The analysis of aqueous mixture suggests that the cinnamon bark contains the important functional groups corresponding to different wavenumbers (as shown in figure no. 8), responsible for reduction of Silver NPs.

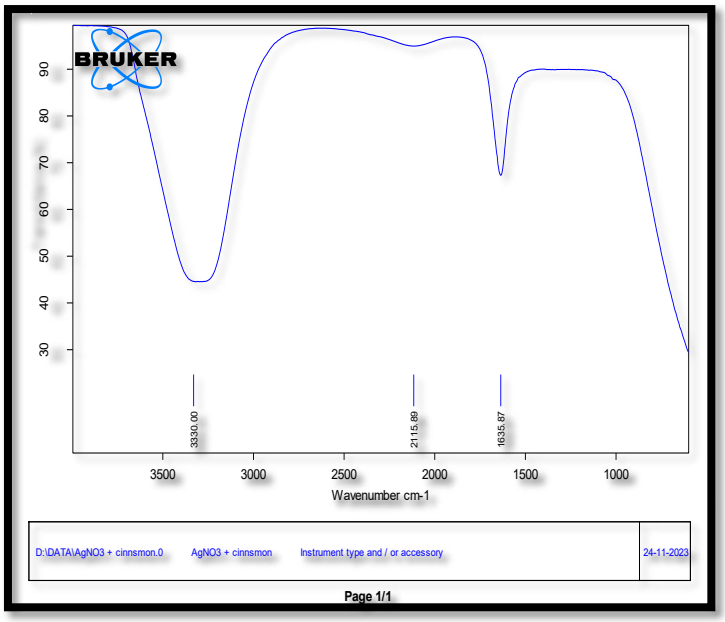

Fig 8 : FTIR analysis

The peak wavenumber at 3330.00 cm^{-1}, 2115.89 cm^{-1}, 1635.87 cm^{-1} corresponds to Phenol group, alkyne and Amide group respectively (Coates,

2000). These functional groups present in the cinnamon bark are responsible for the reduction and stabilization of Silver Nanoparticles. Phenol shows a strong intensity with absorption 60%. All the data has been matched with standard reference.

4) Zeta Potential Analysis – The analysis has been done after about 1 month of the synthesis. Graph at figure no. 9 shows that the Zeta potential of the sample B is -7.65 mV. The negative potential keeps the NPs apart due to the repulsive electric force between them. Reported journal (Vigneshwaran N. et al, 2006) suggests that it is showing average but not an optimum stability. It means particles in aqueous form may agglomerate after a long span of time.

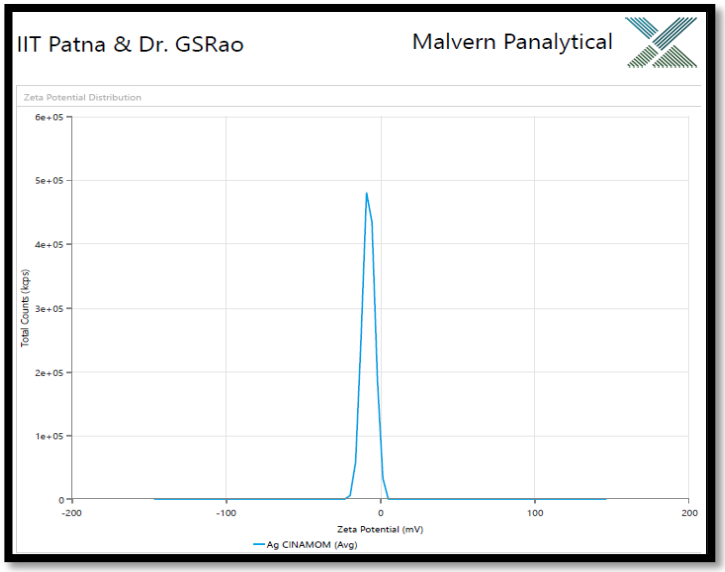

Fig 9: Zeta Potential Analysis

5) Dynamic Light Scattering (DLS) – DLS (Khlebtsov BN et al, 2011) is an important characterization tool that can estimate the NPs size in aqueous form. The analysis has been carried out of sample B (Figure No. 10 A & 10 B), after about 1 month of the synthesis. Particle Size is 287 nm (Statistics Table No. 1). It may be explained as - The particles start to sediment after 1 month of synthesis. Due to this the particles may temporarily stick to agglomerate, showing bigger size particles. The Polydispersity Index (PDI) of the sample is 0.25. It is a good indicator that the particles are largely mono dispersed. Y-intercept at 0.9 in the correlogram shows positive correlation. Also the gradient is moderate, which is showing an appreciable decay rate.

Table No. 1 (DLS Statistics)

Statistics Table

Name	Mean
Z-Average (nm)	287.4
Polydispersity Index (PI)	0.2564
Intercept	0.8926
Fit Error	0.00243

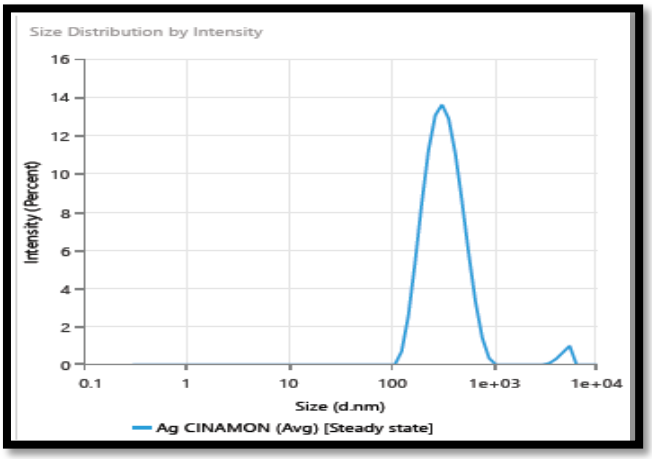

Fig 10 A: DLS Analysis

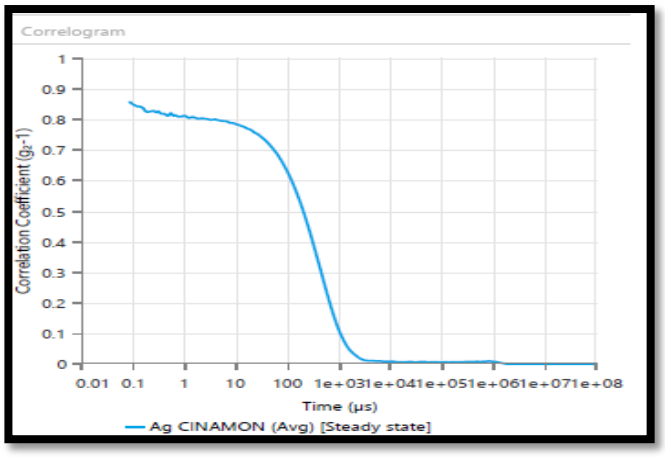

Fig 10 B: DLS Correlogram Analysis

Characterization study in Powder form

Obtaining Powdered Sample

Sample B is centrifuged at 12,000 rpm for 10 min. The sedimented clayey particles are collected and washed twice with Ethanol. Afterward, the particles are heat dried at a constant temperature of 50° C for about 15 min. The powdered form obtained from 500 ml of the prepared sample is about 80 mg. It is here observed that the NPs are still in suspension form in large quantity, which is further need to be left for considerable amount of time to settle down and centrifuge again.

1) X-Ray Diffraction (XRD) Analysis - XRD provides the crystal structure of the material. The crystallography is shown in Figure No. 11. The prominent peaks are found at 38.20°, 44.30°, 64.60° and 77.30°, corresponding to Bragg's reflection planes (termed as hkl indices) (111), (200), (220) and (311) respectively. The peaks are in good agreement with the standard face centred cubic structured Silver XRD diffraction card JCPDS file no. 04-0783 (Lanje et al, 2010). The small extra peaks at 28° and 32.25° may be attributed to the unreduced Silver Nanoparticles . Using Scherer's Equation (A Monshi. Et al, 2009), the crystalline size has been calculated , giving average size to be 10 nm. The covalent radius (Nanoparticle's atomic radius) has been calculated using Bragg's law and Face Centred Cubic crystal (FCC) atomic radius formula, having average value 0.140 nm.

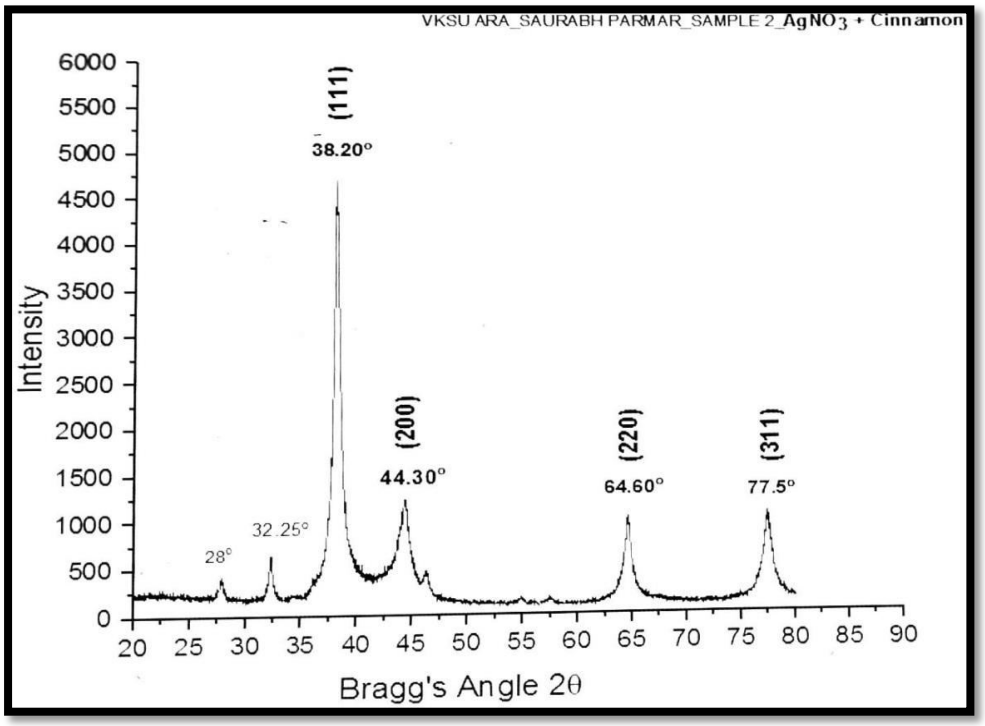

Fig 11: XRD Crystallograph

Peak Angle		Sin θ	Miller Indices		Interplanar Spacing	Lattice Parameter	Covalent radius
2θ°	θ°		hkl	$h^2 + k^2 + l^2$	d (nm)	a (nm)	r (nm)
38.20°	19.10°	0.327	111	3	0.229 nm	0.396 nm	0.140 nm
44.30°	22.15°	0.377	200	4	0.198 nm	0.396 nm	0.140 nm
64.60°	32.30°	0.534	220	8	0.140 nm	0.395 nm	0.139 nm
77.50°	38.75°	0.625	311	11	0.120 nm	0.397 nm	0.140 nm

Scherer's Equation gives the Crystalline diameter (size).

$D = K\lambda / \beta \cos\theta$ ..... (1)

Where, D = Crystal Diameter

K = 0.9

λ = 0.15 nm (X Ray)

β = FWHM (rad)

Peak Angle 2θ	(°)	Intensity	θ (°)	Cos θ	FWHM(°)	FWHM (rad) β	Crystal Diameter (nm)
38.20 °		4711	19.10°	0.94494	0.72	0.0125	11.43 nm
44.30°		1243	22.15°	0.92619	1.56	0.0272	5.35 nm
64.60°		1035	32.30°	0.84526	0.77	0.0134	11.91 nm
77.50°		1043	38.75°	0.77988	1.07	0.0186	9.3 nm

Bragg's Law gives Interplanar spacing:-

$d = n\lambda / 2 \sin\theta$ ..... (2)

Where, d = Interplanar spacing

n = 1

λ = 0.15 nm (x ray wavelength)

Lattice Parameter gives the dimension of FCC cube :-

$a = d \sqrt{(h^2 + k^2 + l^2)}$ ..... (3)

where, a = Lattice Parameter

h,k,l = Miller indices

Covalent radius for FCC structure :-

$r = a / 2\sqrt{2}$ ..... (4)

Where, r = coavalent radius

a = Lattice parameter

2) Field Emission Scanning Electron Microscope (FESEM) Analysis - The powder sample has been observed under FESEM to determine the shape of the synthesized NPs. The observation has been done on different magnifications, as shown in Figure no. 12 (A,B,C,D). It is clear from the images that there is the cluster formation in the NPs. So, Cinnamon synthesized AgNPs are not more stable.

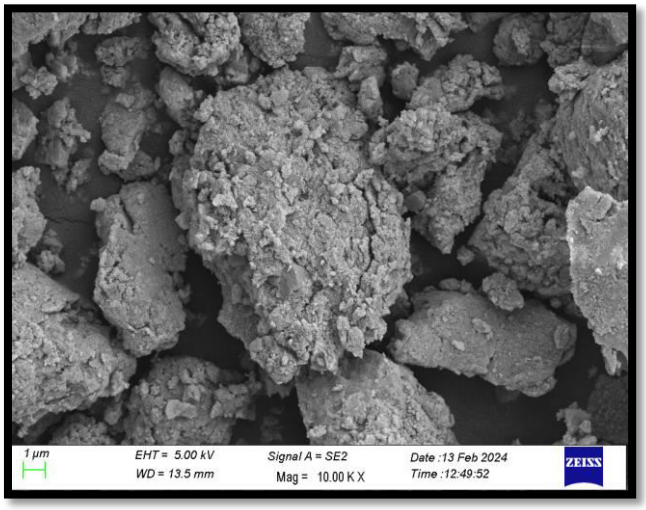

Fig 12 A: FESEM analysis at magnification 10 KX

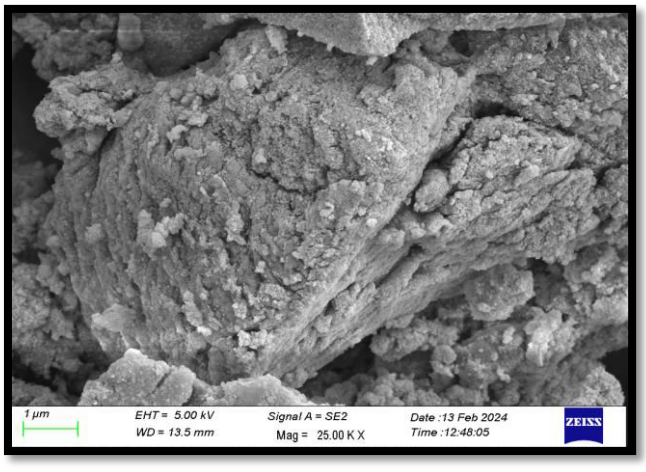

Fig 12 B: FESEM analysis at magnification 25 KX

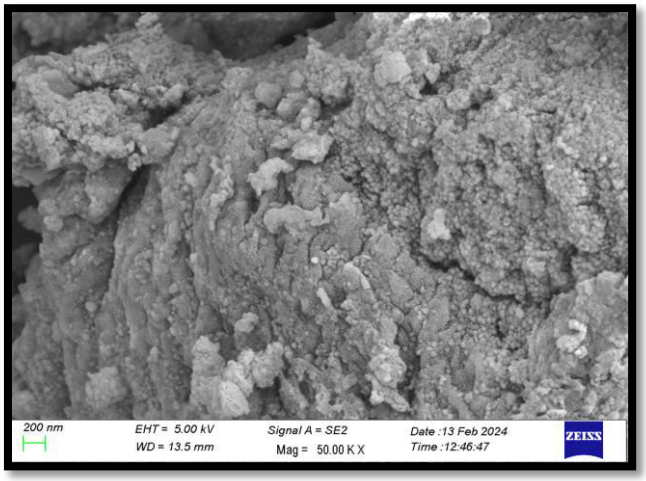

Fig 12 C: FESEM analysis at magnification 50 KX

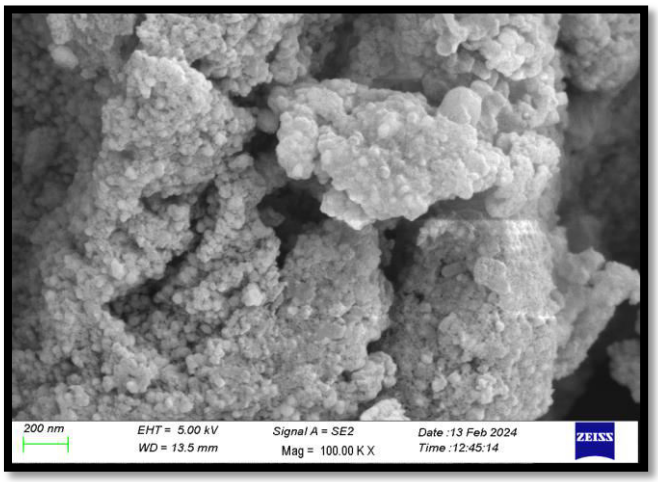

Fig 12 D: FESEM analysis at magnification 100 KX

Energy Dispersive X-ray Spectroscopy (EDX) :- EDX is an analytical technique that enables the elemental analysis of the materials. EDX report (Figure No. 13) suggests that the SEM image contains the NPs of Ag in large amount. But it also can't be denied that the percentage is not in appreciable amount as there are impurities which may be due to unreduced $AgNO_3$, high concentration Cinnamon extract, etc.

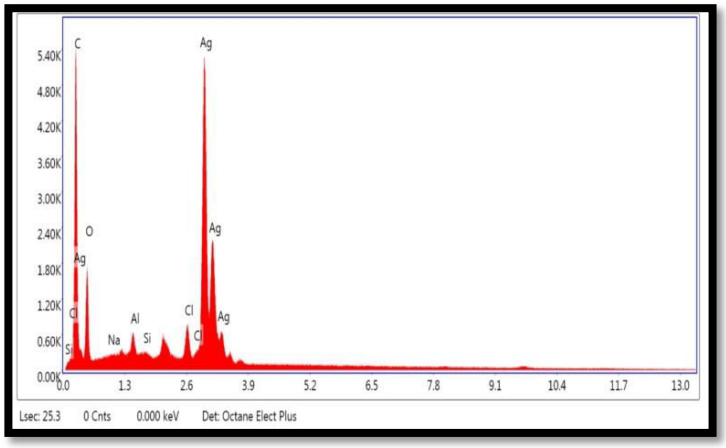

Fig 13 : EDS report

IV. Applications

These cinnamon based synthesized silver nanoparticles can be used in numerous fields (Reidy B et al, 2013). The plasmonic properties of AgNPs can be used in making biosensing and bioimaging devices. Since the capping has been done using natural phytochemicals present in the cinnamon, they are less toxic and efficient in antimicrobial uses. These noble metal nanoparticles show excellent enhanced permeability and retention effect (EPR) due to which they tend to accumulate in tumor tissues. They can accumulate inside the cancerous cells at higher concentrations. Without the aid of exogenous targeting ligands, nanoparticles have been observed to target tumors passively through the EPR (Fan et al, 2023). Thus these synthesized silver NPs can be used in fighting cancer disease.

V. Conclusion

Green synthesized Silver NPs using Cinnamon Bark extract taken in ratio 10:1, is feasible only at high temperature of 60° – 70° C. At room temperature, the reduction is significantly slow. The synthesized AgNPs are not robust in respect to stability and starts agglomerating in aqueous form after the long time of 1 month. The powdered NPs are far better stable but the yielding is very low, with impurities. Further studies may be done to check its adaptability by varying the pH value, increasing the concentration or adding additional reducing agent like glucose, etc.

VI. References

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