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**GREEN SYNTHESIS OF SILVER NANOPARTICLES FROM
CERATOPTERIS THALICTROIDES: SYNTHESIS AND
CHARACTERIZATION**

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ABSTRACT

Green synthesis is now considered as an alternative to chemical and physical synthetic procedures for nanoparticles by using sustainable and eco-friendly materials instead of harsh and toxic chemicals. The aim of the present study describes a cost-effective and environmentally safe technique for green synthesis of silver nanoparticles by using the *Ceratopteris thalictroides* extract as a reducing agent. Further, characterization such as UV-Visible Spectrophotometer, FTIR and XRD analysis were carried out for the synthesized silver nanoparticles. The synthesized silver nanoparticles have maximum absorption at 434nm with an average size of 14 to 126nm. The FTIR data showed prominent peaks in 3411.35, 2923.34, 2853.02, 1721.82, 1623.75, 1384.19, 1271.48, 1193.87, 1102.58, 827.25, 766.95, 644.14, 619.29, 537.52 and 466.09cm⁻¹. The XRD data showed 2θ intense values with various degrees such as 23.7723°, 27.9779°, 28.4961°, 28.5759°, 29.6249°, 32.3826°, 33.9801°, 38.2711°, 40.6193°, 41.3224°, 44.4181°, 46.3463°, 50.3436°, 53.9088°, 57.5331°, 58.8678°, 66.5991°, 67.4111°, 73.8053° and 76.6982°. It could be concluded that the biosynthesis of silver nanoparticles with aqueous extracts of whole plants of *Ceratopteris thalictroides* provides a potential source for the preparation of pharmacologically useful drugs.

Keywords: *Ceratopteris thalictroides*, silver nanoparticles, FTIR, XRD

INTRODUCTION

Nanoparticles have multifunctional properties and have extraordinary applications in medicine, nutrition, and energy [1]. Nanoparticles have created remarkable advantages in the pharmacological industry to cure various bacterial and viral diseases [2]. Among all the noble metal nanoparticles, silver nanoparticles (AgNPs) are the superior product from the field of nanotechnology because of their unique properties such as chemical stability, catalytic, antibacterial, anti-viral, antifungal and anti-inflammatory activities [3].

Several techniques are available for the synthesis of silver nanoparticles like ion sputtering, chemical reduction, and sol-gel, etc., unfortunately, many of the nanoparticles syntheses methods involved the use of hazardous chemicals or high energy requirements [3]. Green synthesis is now considered as an alternative to chemical and physical synthetic procedures for nanoparticles by using sustainable and eco-friendly materials instead of harsh and toxic chemicals. The rich biodiversity and easy availability of plant entities have been highly explored for nanoparticle synthesis [4]. Crude extracts of plants contain novel secondary metabolites such as phenolic acids, flavonoids, alkaloids, and terpenoids. These compounds are mainly responsible for the reduction of ionic into bulk metallic

nanoparticle formation [5]. The present study is the first for the green synthesis of silver nanoparticles by using whole plants of *Ceratopteris thalictroides*.

Ceratopteris thalictroides, a pteridophyte, occurs in semi-shaded localities mostly rooted in mud, occasionally free-floating and common in paddy fields, ponds [6-8]. The fronds of *C. thalictroides* are used as a vegetable [9, 10]. The fronds of *C. thalictroides* are used as a poultice in skin diseases [11]. The uncurled fronds are eaten as a salad or as a substitute for asparagus. The tribal people use the plant as a poultice for skin problems [12]. The whole plant parts are ground into a paste and mixed with turmeric. The mixture is applied to the affected places to treat cure skin diseases and wounds [13, 14]. In Madagascar *C. thalictroides* leaves are eaten as a salad or cooked as a vegetable; whereas in Swaziland, leaves are eaten as a leafy vegetable [15]. Because of the above, in the present study, the plant-mediated synthesized AgNPs were characterized and studied in detail with all of their properties significant to current science and prevailing technologies.

MATERIALS AND METHODS

Preparation of plant extracts:

Fresh whole plants of *Ceratopteris thalictroides* (L.) Brongn., were collected from Puthalam (8.106488; 77.46),

Kanyakumari district, Tamil Nadu, India and was authenticated at Botanical Survey of India, Southern Circle, Coimbatore. The voucher specimen (Voucher No. VS-VV-01) was also maintained in the Department of Botany, V.O. Chidambaram College, Tuticorin, Tamil Nadu, India. Fresh and healthy plants were collected and rinsed thoroughly first with tap water followed by distilled water to remove all the dust and unwanted visible particles, cut into small pieces and dried at room temperature. About 10g of finely chopped plant materials were added in a conical flask containing 100ml of double distilled water and boiled for about 20min. The extracts were then filtered thrice through Whatman No. 1 filter paper to remove particulate matter and to get clear solutions which were then refrigerated (4°C) in 250ml Erlenmeyer flasks for further experiments. In every step of the experiment, sterility conditions were maintained for the effectiveness and accuracy of results without contamination [16].

Silver nanoparticle (Ag NP) synthesis:

For the synthesis of silver nanoparticles, 5ml of plant extract was mixed with 95ml of 1mM aqueous silver nitrate solution. This setup was incubated in a dark chamber to minimize photo-activation of silver nitrate at room temperature. The reduction of Ag^+ to Ag^0 was confirmed by the colour change of the

solution from greenish-yellow to red [17]. 50ml of colloidal silver nanoparticle suspension was stored in the refrigerator (4°C) for further studies like UV-Visible spectrophotometer spectral analysis. The remaining suspension was poured into a Petridis and kept at $80^\circ\text{C} \pm 2$ for 12h in the hot-air oven for drying. The dried sample was scraped for FTIR analysis.

Characterization of silver nanoparticles:

UV-Visible spectroscopy:

To observe the optical property of biosynthesized silver nanoparticles, 1ml of the colloidal silver nanoparticle suspension was taken in a test tube and was diluted with 2ml of deionized water. Then the sample was scanned in UV-visible spectrophotometer (Shimadzu UV 1800 UV-VIS spectrophotometer) at room temperature operated at a resolution of 1nm between 190 to 1100nm range [18].

Fourier transform infrared spectroscopy (FTIR):

Fourier-transform Infrared (FTIR) spectroscopic analysis of the dried silver nanoparticles was carried out by the potassium bromide (KBr) pellet method. 1mg of silver nanoparticles were mixed with 100mg of dry potassium bromide (1:100 ratio) and then the mixture was compressed into a pellet using a hydraulic press (5000-10000 PSI). The compressed pellet was put into the sample holder and the FTIR (Systronics 166) spectra were

recorded in the range of 400-4000 cm^{-1} . To alleviate the moisture content in the sample, a blank disc was put in the reference beam [19].

X-ray diffraction study (XRD):

The colloidal silver nanoparticle suspension stored in the refrigerator was centrifuged at 15000rpm for 10min. The supernatant was discarded and the pellet was retained. The pellet was re-dissolved in 10ml of de-ionized water. While preparing samples for X-Ray Diffraction (XRD) analysis, a thin film of a sample (100 μl) was applied on a glass slide and allowed to dry for 30min. The XRD pattern was recorded using X'Pert PROP Analytical-PW 3040/60 X-ray Diffractometer with an operating voltage of 30kV at a 20mA current strength. The sample was subjected to Cu K α radiation (K α 1.54056 \AA) with nickel monochromator in the 2θ range of 20–80° [20]. The size of the silver nanoparticle was calculated by Debye–Scherrer equation [21] as follows:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where: D is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; k is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite; λ is the X-ray wavelength ($\lambda = 1.54056 \text{ \AA} =$

0.154056nm); β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta(2\theta)$; θ is the Bragg angle.

RESULTS AND DISCUSSION

In this present investigation, we developed an inexpensive, versatile and very reproducible method for the synthesis of silver nanoparticles using the plant extract of *Ceratopteris thalictroides*. An aqueous solution of 1mM silver nitrate when mixed with extract of *C.thalictroides*, a visible colour change from greenish-yellow to brown was noted within 5min at room temperature. Reduction of silver ions exhibited brown colour in aqueous solution due to surface plasma vibration in silver nanoparticles. When the plant extract was added to an aqueous solution of silver ion complex, the colour started to change from green to brown due to the reduction of silver ions [22].

The formation of silver nanoparticles was confirmed by UV-visible spectroscopy analysis. UV-visible spectrum analysis for the biosynthesized silver nanoparticles using the extracts of *C.thalictroides* shows a peak at 434nm (Figure 1). In an earlier study, characteristic and well-defined surface plasmon resonance (SPR) band at 414nm obtained for the silver nanoparticles

synthesized by using *Calliandrahae matocephala* extract as reducing agent confirms the formation of silver nanoparticles [17].

The FTIR spectroscopy analysis of *Ceratopteris thalictroides* extract with 1mM silver nitrate solution shows peaks at 3411.35cm^{-1} , 2923.34cm^{-1} , 2853.02cm^{-1} , 1721.82cm^{-1} , 1623.75cm^{-1} , 1384.19cm^{-1} , 1271.48cm^{-1} , 1193.87cm^{-1} , 1102.58cm^{-1} , 827.25cm^{-1} , 766.95cm^{-1} , 644.14cm^{-1} , 619.29cm^{-1} , 537.52cm^{-1} and 466.09cm^{-1} absorption peaks are known to be associated with the stretching vibration for N-H stretch, C-H stretch, C-H stretch, C=C stretch, C = C stretch, C = H bend, C - O stretch, C - O stretch, C - O stretch, C = C bend, C-Cl stretch, C - H bend, C - H bend, C - I stretch and S - S stretch, respectively (**Figure 2 and Table 1**).

The absorbance bands observed with *Ceratopteris thalictroides* extract at around 3411.35cm^{-1} (amine arising due to N-H stretch in proteins), suggest the presence of proteins on the surface of Ag-core particles, and plant proteins in the NPs shell. As plant molecules get absorbed onto the AgNPs surface, the amine groups intend to form stronger bonds with Ag atoms, which will break most of the H-bonds between the N-H groups and lead the narrowing and blue shifts of the amine bond. These results confirm the presence of

possible proteins acting as reducing and stabilizing agents [23].

X-ray diffraction is a method of determination of the crystallinity of a compound. Here, to find the crystalline nature of the biosynthesized silver nanoparticles with *Ceratopteris thalictroides* extract, the XRD analysis was done. The XRD pattern clearly showed that the plant extract mediated synthesized silver nanoparticles were crystalline and the average size of nanoparticles was calculated as 35nm (**Figure 3 and Tables 2 and 3**).

The X-ray diffractogram of *Ceratopteris thalictroides* extract mediated synthesized silver nanoparticles showed peaks in the whole spectrum of $2\theta^\circ$ values of 23.7723° , 27.9779° , 28.4961° , 28.5759° , 29.6249° , 32.3826° , 33.9801° , 38.2711° , 40.6193° , 41.3224° , 44.4181° , 46.3463° , 50.3436° , 53.9088° , 57.5331° , 58.8678° , 66.5991° , 67.4111° , 73.8053° and 76.6982° and these peaks were understood to be (1 1 1), (2 0 0), (2 0 0), (2 1 0), (2 1 0), (2 1 1), (2 2 0), (2 2 1), (2 2 1), (3 1 0), (3 1 1), (3 2 0), (3 2 1), (4 0 0), (4 1 0), (4 2 1), (4 2 1) and (5 0 0) lattice planes respectively, to the face-centered cubic (fcc) structure of metallic silver. This is in accordance with the standard metallic silver XRD pattern JCPDS No. 04-0873. The intense diffraction peak of (111) substantiated that the synthesized silver nanoparticles might be enriched with (111) facets [17].

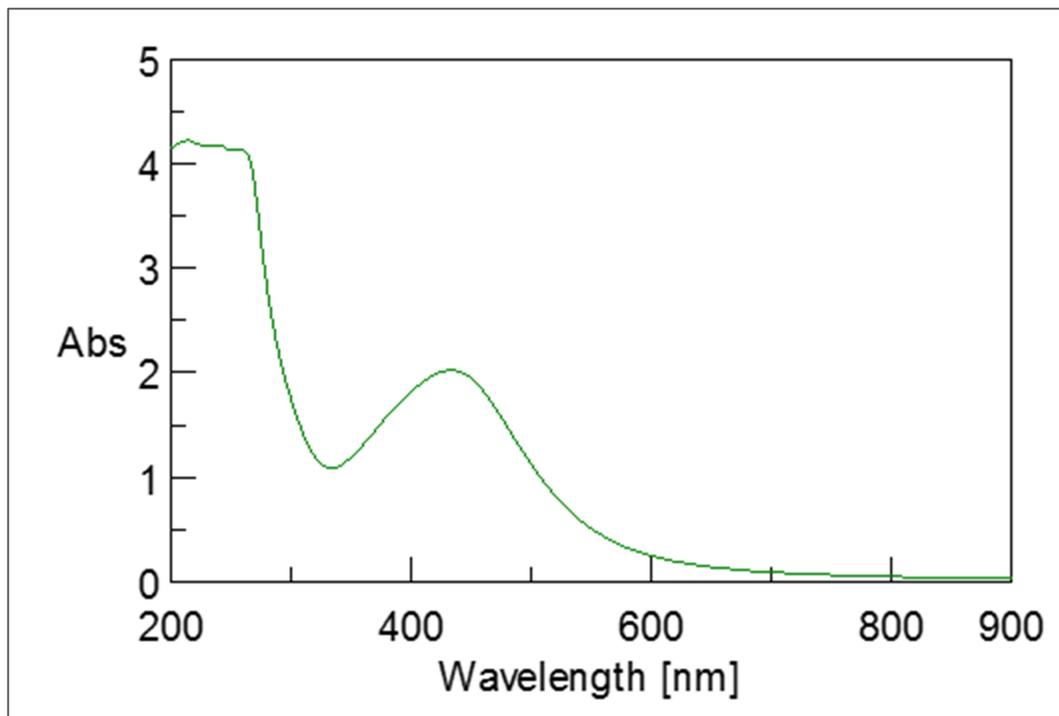


Figure 1: UV-Vis absorption spectrum of *Ceratopteris thalictroides* AgNPs

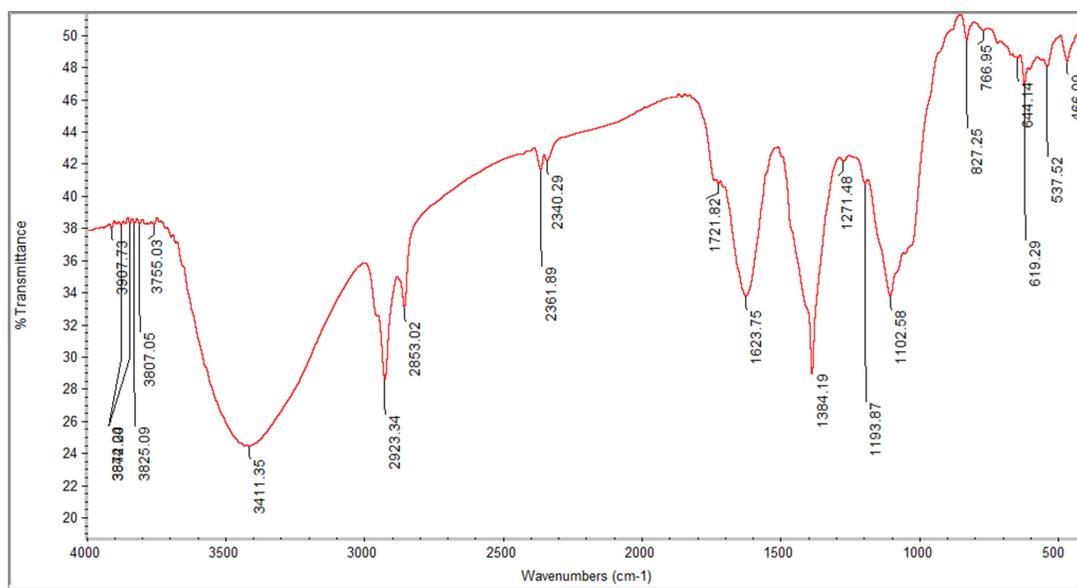


Figure 2: FTIR spectrum of *Ceratopteris thalictroides*

Table 1: FTIR spectral qualities interpretation of the comparative shift in functional peaks of critical value (*Ceratopteris thalictroides*)

Frequency absorption (cm-1)	Group	Compound class
3907.73	---	---
3840.00	---	---
3825.09	---	---
3807.05	---	---
3755.03	---	---
3411.35	N - H stretching	Primary amine
2923.34	C - H stretching	Alkane
2361.89	---	---
2340.29	---	---
1721.82	C = O stretching	Aldehyde
1623.75	C = C stretching	Alkane
1384.19	C = H bending	Alkane
1271.48	C - O stretching	Alkyl aryl ether
1193.87	C - O stretching	Ester
1102.58	C - O stretching	Secondary alcohol
827.25	C = C bending	Alkene
766.95	C - Cl stretching	Halo Compound
644.14	C - H bending	Alkyne
619.29	C - H bending	Alkyne
537.52	C - I stretching	Aliphatic iodo compounds
466.09	S - S stretching	Aryl disulfides

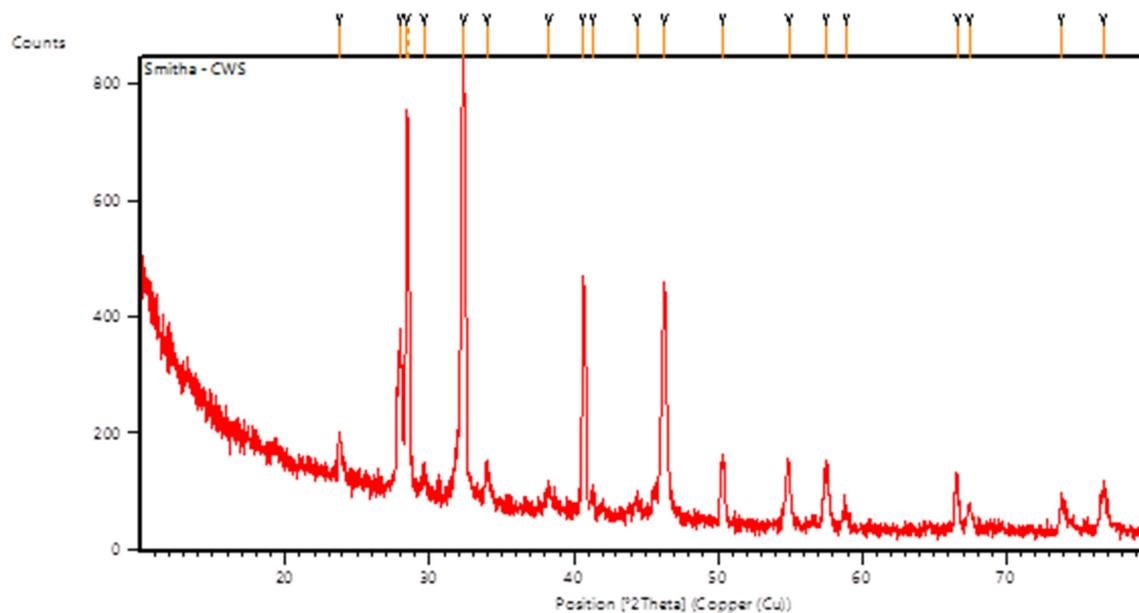


Figure 3: XRD analysis of biosynthesised silver nanoparticles using *Ceratopteris thalictroides*

Table 2: Peak indexing from XRD spectra of *Ceratopteris thalictroides*

2θ	θ	Sin θ	Sin ² θ	$\frac{3 \times \text{Sin}^2 \theta}{\text{Sin}^2 \theta_{\min}}$	h ² +k ² +l ²	h k l
23.7723	11.8861	0.2060	0.0424	$\frac{3 \times 0.0424}{0.0424} = 3$	1 ² +1 ² +1 ²	1 1 1
27.9779	13.9889	0.2417	0.0584	$\frac{3 \times 0.0584}{0.0424} = 4$	2 ² +0+0	2 0 0
28.4961	14.2480	0.2461	0.0606	$\frac{3 \times 0.0606}{0.0424} = 4$	2 ² +0+0	2 0 0
28.5759	14.2879	0.2468	0.0609	$\frac{3 \times 0.0609}{0.0424} = 4$	2 ² +0+0	2 0 0
29.6249	14.8124	0.2557	0.0653	$\frac{3 \times 0.0653}{0.0424} = 5$	2 ² +1 ² +0	2 1 0
32.3826	16.1913	0.2788	0.0777	$\frac{3 \times 0.0777}{0.0424} = 5$	2 ² +1 ² +0	2 1 0
33.9801	16.9900	0.2922	0.0854	$\frac{3 \times 0.0854}{0.0424} = 6$	2 ² +1 ² +1 ²	2 1 1
38.2711	19.1355	0.3278	0.1074	$\frac{3 \times 0.1074}{0.0424} = 8$	2 ² +2 ² +0	2 2 0
40.6193	20.3096	0.3471	0.1205	$\frac{3 \times 0.1205}{0.0424} = 9$	2 ² +2 ² +1 ²	2 2 1
41.3224	20.6612	0.3528	0.1245	$\frac{3 \times 0.1245}{0.0424} = 9$	2 ² +2 ² +1 ²	2 2 1
44.4181	22.2090	0.3780	0.1429	$\frac{3 \times 0.1429}{0.0424} = 10$	3 ² +1 ² +0	3 1 0
46.3463	23.1731	0.3935	0.1549	$\frac{3 \times 0.1549}{0.0424} = 11$	3 ² +1 ² +1 ²	3 1 1
50.3436	25.1718	0.4253	0.1809	$\frac{3 \times 0.1809}{0.0424} = 13$	3 ² +2 ² +0	3 2 0
53.9088	26.9544	0.4533	0.2055	$\frac{3 \times 0.2055}{0.0424} = 14$	3 ² +2 ² +1 ²	3 2 1
57.5331	28.7665	0.4812	0.2316	$\frac{3 \times 0.2316}{0.0424} = 16$	4 ² +0+0	4 0 0
58.8678	29.4339	0.4814	0.2415	$\frac{3 \times 0.2415}{0.0424} = 17$	4 ² +1 ² +0	4 1 0
66.5991	33.2995	0.5490	0.3014	$\frac{3 \times 0.3014}{0.0424} = 21$	4 ² +2 ² +1 ²	4 2 1
67.4111	33.7055	0.5549	0.3079	$\frac{3 \times 0.3079}{0.0424} = 21$	4 ² +2 ² +1 ²	4 2 1
73.8053	36.9026	0.6004	0.3605	$\frac{3 \times 0.3605}{0.0424} = 25$	5 ² +0+0	5 0 0
76.6982	38.3491	0.6204	0.3849	$\frac{3 \times 0.3849}{0.0424} = 27$	5 ² +1 ² +1 ²	5 1 1

Table 3: Particle size derived from XRD Spectra of *Ceratopteris thalictroides*

S.No	h k l	2θ	θ	FWHM (°)	β (radiation)	Size (nm)
1	1 1 1	23.7723	11.8861	0.2007	0.0034	42
2	2 0 0	27.9779	13.9889	0.3011	0.0052	28
3	2 0 0	28.4961	14.2480	0.0816	0.0014	99
4	2 0 0	28.5759	14.2879	0.0612	0.0011	126
5	2 1 0	29.6249	14.8124	0.3264	0.0057	25
6	2 1 0	32.3826	16.1913	0.2448	0.0042	34
7	2 1 1	33.9801	16.9900	0.4080	0.0071	20
8	2 2 0	38.2711	19.1355	0.2448	0.0042	35
9	2 2 1	40.6193	20.3096	0.0612	0.0011	14
10	2 2 1	41.3224	20.6612	0.2448	0.0042	35
11	3 1 0	44.4181	22.2090	0.4896	0.0085	17
12	3 1 1	46.3463	23.1731	0.4080	0.0071	21
13	3 2 0	50.3436	25.1718	0.3264	0.0057	27
14	3 2 1	53.9088	26.9544	0.3264	0.0057	28
15	4 0 0	57.5331	28.7665	0.4080	0.0071	22
16	4 1 0	58.8678	29.4339	0.3264	0.0057	28
17	4 2 1	66.5991	33.2995	0.2856	0.0050	34
18	4 2 1	67.4111	33.7055	0.3264	0.0057	29
19	5 0 0	73.8053	36.9026	0.4080	0.0071	24
20	5 1 1	76.6982	38.3491	0.5712	0.0099	19
Mean						35

CONCLUSION

A plant-mediated, green method of synthesizing silver nanoparticles was successfully performed by employing the extract of *Ceratopteris thalictroides*. The synthesized nanoparticles were characterized by UV-Vis spectrophotometer, FTIR and XRD methods of analysis. These analyses confirmed the reduction of Ag^+ ions to Ag^0 which is supposed through the plant extract as capping agents i.e., the phytochemical constituents found in this plant are acting as the reducing agents. It could be concluded that the biosynthesis of silver nanoparticles with aqueous extracts of *Ceratopteris thalictroides* provides a potential source for the preparation of pharmacologically useful drugs.

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