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ENVIRONMENTAL BENIGN ROUTE IN THE SYNTHESIS OF PALLADIUM NANOPARTICLES USING LEAVES OF *ACALYPHA INDICA* L.

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ABSTRACT

We report the environmental benign route in the synthesis of palladium nanoparticles using the aqueous leaf broth of *Acalypha indica* L. In this protocol, the biomolecules present in the leaf broth, reduced palladium ions into palladium nanoparticles and these biomolecules also acted as capping and stabilizing agents. The colour change in the reaction medium from pale yellow to dark brown during the incubation period indicated the synthesis of palladium nanoparticles. Further, we used the following analyses to characterize the palladium nanoparticles- UV-Visible spectroscopy, X-ray diffraction patterns (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) patterns. This protocol of synthesis of palladium nanoparticles using leaf broth of *Acalypha indica* L. becomes environmental benign route, simple, cost effective as it does not involve any toxic chemicals. Hence, this green approach of this method makes it as an alternative route to physical and chemical methods.

KEYWORDS: Palladium nanoparticles, *Acalypha indica* L., Reaction medium, Leaf broth, biomolecules.

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INTRODUCTION

Nanotechnology is one of the major breakthroughs of modern science, enabling materials of distinctive size, structure and composition to be formed[1]. An important area of research in nanotechnology deals with the synthesis of metallic nanoparticles[2]. Metal nanoparticles form a bridge between bulk material and atomic (or) molecular structures[3]. Physical and chemical methods have been used to synthesize the metal nanoparticles[4-7], which are toxic and harmful to environment. Hence, the biological methods have been emerged, which utilize various biological systems such as bacteria, fungus and plant extracts for the synthesis of metal nanoparticles[8-12]. Among them, various higher plants were exploited for the synthesis of different types of metal nanoparticles such as silver, gold and palladium and those were simple and versatile processes[9,13-18,12]. The higher plants have higher rate of reduction of metal ions than the micro-organisms and also they do not need laborious maintenance of culture[19,20]. However, the biological synthesis of palladium nanoparticles using plant extract has not established as much as for silver and gold nanoparticles[12]. There are few reports available for the biological synthesis of palladium nanoparticles. *Diopyros kaki* leaf[17], *Cinnamom zeylanicum* bark[21], *C. camphora* leaf[22], *Curcuma longa* tuber[23], banana peel[24] and Soybean leaf extract[12] were used as reducing as well as stabilizing agents in the synthesis of palladium nanoparticles[12]. We have exploited the leaves of *Merremia tridentata*[25]; *Odina wodier*[26]; *Hyptis suaveolens*[27]; *Tecoma stans*[28]; *Eucalyptus globulus*[29]; Manilkara *zapota* and *Mimusops elengi*[30] for the synthesis of silver nanoparticles. We have also used a seaweed *Kappaphycus alavarezii*[31] for the synthesis of silver nanoparticles. In continuation of these efforts to bring out the environmental benign route in the synthesis of palladium nanoparticles through green approach, we have exploited leaves of *Acalypha indica*.

MATERIALS AND METHODS

All the reagents used in the present study were obtained from Himedia laboratories Pvt. Ltd., (Mumbai, India). *Acalypha indica* L. (Family: *Euphorbiaceae*), is a higher plant having catkin type of inflorescence. It occurs in India, Sri Lanka, Yemen, Pakistan and throughout tropical Africa and South Africa. It has possibly been introduced elsewhere as a weed. In West and East Africa the plant is used as a medicinal plant. It is a common herb used as medicinal plant, growing up to 75 cm tall with ovate leaves. Flowers are green, unisexual found in catkin inflorescence. In West Africa the leaves are cooked and eaten as a vegetable. This plant is held in high esteem in traditional Tamil Siddha medicine as it is believed to rejuvenate the body[32]. We collected the fresh and healthy leaves of *Acalypha indica* L. (Fig. 1) from the campus of Ayya Nadar Janaki Ammal College, Sivakasi, Tamil Nadu, India. The collected leaf samples were thoroughly washed with tap water followed by distilled water to remove the surface contaminants and dried for 48 hours under shade. The dried leaves (10g) were ground to make fine powder using mortar and pestle and sieved using 20 mesh sieves to get uniform size range. For the preparation of leaf broth, the sieved leaf powder of *Acalypha indica* (10g) added to 100ml of distilled water and boiled at 70^0C for ten minutes. The freshly prepared leaf broth (10ml) was re-suspended in 90ml of aqueous solution of palladium chloride and this mixture is used was palladium reaction medium (PRM). This PRM was kept in an Incubator cum shaker (Orbitek) at 250rpm for 24 hours.

Figure 1
Acalypha indica L. Leaves

An aliquot of reaction medium was collected after the centrifugation at 5000rpm for 10min using a cooling centrifuge (REMI). These aliquots were characterized using the following analyses: UV-Visible spectroscopy (UV-Vis), Fourier Transform Infra-Red Spectroscopy (FTIR), X-ray diffraction (XRD) analysis, Scanning Electron Microscopy (SEM) and Energy Dispersive X- ray analysis (EDX).

3. RESULTS AND DISCUSSION

In this present study, we have shown the ability of *Acalypha indica* leaf broth to reduce palladium chloride ions and produce palladium nanoparticles, as an environmental benign route.

1. UV-Visible spectrum of Palladium nanoparticles

The PRM exhibited the gradual colour change from transparent yellow to brown (Fig. 2 inset), which was due to the vibrations of Surface Plasmon Resonance (SPR). It indicates the formation of palladium nanoparticles. The intensity of the colour arises from the surface plasmon, which are dipole oscillations arising when an electromagnetic field in the visible range is coupled to the collective oscillations of conduction electrons[33,19]. Fig. 2 shows the UV-Vis spectra of PRM with respect to different time intervals for 24 hours. The λ max was observed at 420nm and the absorbance was raised up to 0.52a.u. The λ max of palladium nanoparticles synthesized using an aqueous fruit extract of *Pistacia atlantica* was 380nm[34], while it was 420nm in case of palladium nanoparticles synthesized by soybean (*Glycine max*) leaf extract[12]. With the increase the particle size, the optical absorption spectra of metal nanoparticles that are dominated by SPR may shift towards longer wavelengths[19]. Yang *et al.*[22] ascribed the absorption bands appearing in the contrast spectrum of Palladium chloride solution to the ligand-to-metal charge-transfer transition of Pd (II) ions[35-37].

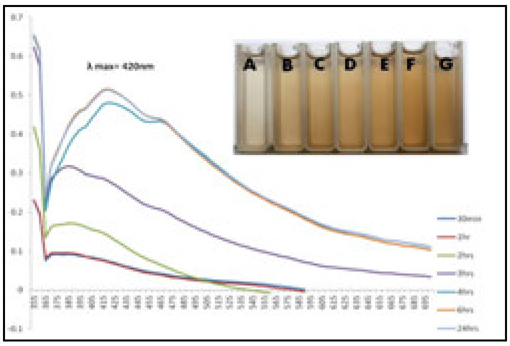

Figure 2
UV –Visible absorption spectra of palladium reaction medium at different time intervals. The inset shows the colour change of the reaction medium- A-30min, B-1hr, C-2hrs, D-3hrs, E-4hrs, F-6hrs, and G-24hrs.

2. FT-IR Spectroscopic Analysis

The IR spectral analysis was performed using Shinmadzu FT-IR spectrophotometer through KBR pellet method. FTIR measurements identified the biomolecules in the leaf broth of *Acalypha indica*, which are responsible for reduction and stability to the biosynthesized palladium nanoparticles. Fig. 3 shows the FT-IR spectral bands at 3927.07 cm^{-1} corresponds to N-H stretch (amines), 3757.33 cm^{-1} corresponds to OH stretch (carboxylic acids), 3425.58 cm^{-1} corresponds to C-H stretch (alkyls), 2916.37 cm^{-1} corresponds to C-H stretch (alkanes), 2854.65 cm^{-1} corresponds to C≡N stretch (nitriles), 2283.72 cm^{-1} corresponds to C=O stretch (esters), 1720.50 cm^{-1} corresponds to N-H bend (primary amines), 1635.64 cm^{-1} corresponds to N-O asymmetric stretch (nitro compounds), 1543.05 cm^{-1} corresponds to C-H bend (alkanes), 1458.18 cm^{-1} corresponds to C-C stretch (aromatics), 1404.18 cm^{-1} corresponds to C-N stretch (aliphatic amines), 1242.16 cm^{-1} corresponds to C-O stretch (alcohols), 1080.14 cm^{-1} corresponds to C-Cl stretch (alkyl halides), 779.24 cm^{-1} corresponds to C-H bend (alkenes), 655.80 cm^{-1} and 424.34 cm^{-1} correspond to C-I stretch (alkyl halides). The bioreduction of palladium ions may be due to the major involvement of tyrosine during the synthesis of palladium nanoparticles[12], while Kanchana *et al*. (2010)[19] reported that it may be due to either carbonyl groups or secondary amines.

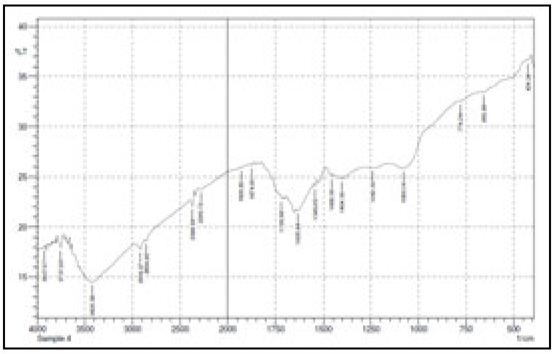

Figure 3
FTIR spectrum of palladium reaction medium

3. XRD analysis

Crystallite metallic palladium nanoparticles were examined by X-ray diffractometer Shimadzu (XRD 6000). The X-ray pattern of synthesized palladium nanoparticles was shown in Fig.4. The strong Bragg's diffracted peaks were observed at 28.2^{o} and 40.4^{o} which correspond to the (100) and (111) facets of the face-centered cubic lattice of palladium. The crystallite size of palladium nanoparticles was calculated with the help of peak broadening profile of (111) peak at 40.4^{o} using Scherrer's formula. The calculated crystallite size of the synthesized palladium nanoparticles is 70nm.

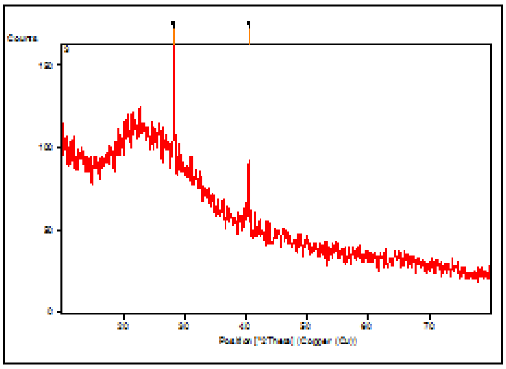

Figure 4
XRD pattern of palladium reaction medium

4. SEM and EDX analysis

SEM images provided information about the morphology and size of the biosynthesized palladium nanoparticles. Fig. 5 shows the SEM image of palladium nanoparticles. SEM measurements explained that the palladium nanoparticles were in different shapes such as relatively spherical and cubic within the size range of 50-70nm. Kanchana *et al.* (2010)[19] reported that the synthesized palladium nanoparticles using *Solanum trilobatum* leaf extract were spherical in shape within the size range of 60-70nm. Molaie *et al.* (2012)[34] fabricated the spherical shaped palladium nanoparticles with an average size of about 60nm using aqueous fruit extract of *Pistacia atlantica*. Fig. 6 shows the EDX patterns of synthesized palladium nanoparticles using *Acalypha indica* leaf extract. The EDX patterns of PRM confirm the presence of palladium nanoparticles.

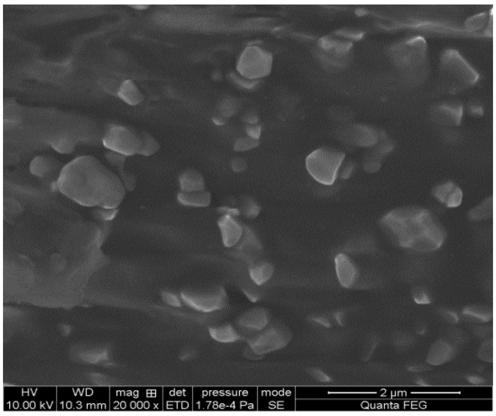

Figure 5
SEM images of palladium reaction medium

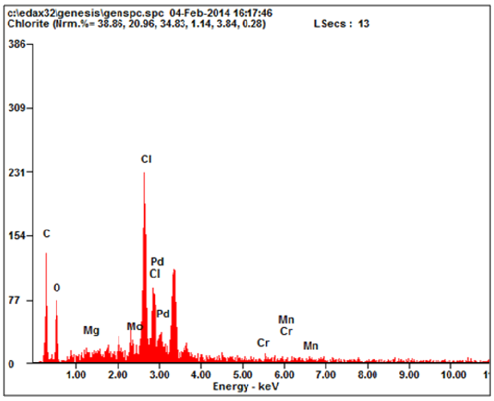

Figure 6
EDX patterns of palladium reaction medium showing the presence of palladium

CONCLUSION

Thus we reported the environmental benign route in the synthesis of palladium nanoparticles through rapid reduction of palladium chloride with a help of *Acalypha indica* leaf broth. The PRM changed its color from transparent yellow to brown during the incubation period. The UV-Visible spectrum of the PRM has λ max at 420 nm and the absorbance was raised up to 0.52a.u. The FT-IR spectrum showed the bands at 3927.07 cm^{-1}, 3757.33 cm^{-1}, 3425.58 cm^{-1}, 2916.37 cm^{-1}, 2854.65 cm^{-1}, 2283.72 cm^{-1}, 1720.50 cm^{-1}, 1635.64 cm^{-1}, 1543.05 cm^{-1}, 1458.18 cm^{-1}, 1404.18 cm^{-1}, 1242.16 cm^{-1}, 1080.14 cm^{-1}, 779.24 cm^{-1}, 655.80 cm^{-1} and 424.34 cm^{-1} after bio-reduction. The synthesized particles ranged in size from 50-70 nm and were in different shapes such as relatively spherical and cubic as shown by the SEM images. The strong palladium peak obtained in the EDX patterns confirms the significant presence of elemental palladium. The XRD analysis determines the average size of the nanoparticles is 70 nm. This green approach becomes a simple, cost-effective and an environmental benign route in the synthesis of palladium nanoparticles which may be an alternative to physical and chemical methods.

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