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GREEN SYNTHESIS OF PALLADIUM NANOPARTICLES USING Coleus *amboinicus* Lour.

B.S. NAVEEN PRASAD*[1], T.V.N. PADMESH*[2], V. GANESH KUMAR[3] AND K. GOVINDARAJU[3]

[1]Department of Chemical Engineering, Sathyabama University, Chennai – 600119, India
[2]Department of Chemical Engineering, Manipal International University, Nilai, Malaysia
[3]Nanoscience Division, Centre for Ocean Research, Sathyabama University, Chennai-600119, India

ABSTRACT

Phytochemical based synthesis of palladium nanoparticles by bioreduction of medicinally potent plant extract *Coleus amboinicus* is investigated in the present study. Treatment of palladium chloride with *Coleus amboinicus* extract resulted in the formation of palladium nanoparticles. The formation of palladium nanoparticles were confirmed using UV-vis, FTIR, TEM and XRD. Polyols such as flavones, terpenoids and polysaccharides would be involved in bioreduction of metallic Pd (II) to Pd (0). The nanoparticles were spherical and triangular in shape with size ranging from 10-28 nm.

KEYWORDS: ***Coleus amboinicus;*** **biomaterials; palladium nanoparticles; electron microscopy**

B.S. NAVEEN PRASAD
Department of Chemical Engineering, Sathyabama University, Chennai – 600119, India

***Corresponding author**

INTRODUCTION

Biosynthesis of palladium nanoparticles (PdNPs) using natural products is an emerging field in nanoscience research. Palladium has extensive applications in electronic industry, dental alloys, magnetic materials and are also used as hydrogenation catalysts. In recent years PdNPs are of great interest due to their applications that differs from those of bulk palladium metals and noble metals[1] due to their large surface area. PdNPs plays a key role in various industrial applications concerned with low–temperature reduction of automobiles[2], hydrogen storage[3], gas sensing[4] and catalysis[5]. Chemical reduction in aqueous or non-aqueous solutions, micro–emulsions template and ultrasonic assisted methods are conventional methods[6] for metal nanoparticles. Size and shape controlled synthesis of PdNPs have also been carried out using hydrothermal methods, photochemical methods, seed–mediated growth methods, polyol reduction methods and thermal decomposition methods[7]. Utilization of biological sources has been the most efficient method involving synthesis of nanoparticles and has gained considerable attention in recent years[8-10]. PdNPs were synthesized using leaf extract of *Delonix regia* and their catalytic activity was evaluated[11]. Biosynthesis of PdNPs were demonstrated using antioxidants present in *Gardenia jasminoides* Ellis and its efficiency as a nano catalyst for p–nitrotoluene hydrogenation was tested [12]. *Coleus amboinicus* of *Coleus*, family is a common herb in India and is well known for its antimicrobial and pharmacological values. It possesses antioxidant properties and it is also used to cure tumours[13] bronchitis, asthma, chronic cough, epilepsy etc,[14-16]. The present investigation involves the reaction of polyols present in the leaf extract such as flavones, terpenoids and polysaccharides play a vital role in the reduction of Pd (II) ions.

MATERIALS AND METHODS

Materials

Palladium chloride ($PdCl_2$) was purchased from SRL Pvt. Ltd., India and used as received. All other reagents used were of analytical grade with maximum purity. The fresh leaves of *C. amboinicus* were collected from Sathyabama University campus, Chennai and were cleaned with double distilled water.

Synthesis of PdNPs

1 g of fresh leaves were finely grounded and made up to 100 mL with double distilled water. Different concentrations of 1 mM $PdCl_2$ and plant extract (90:10, 80:20, 70:30, 60:40, 50:50) were subjected to various pH (3,4,5,6,8 and 9) at room temperature.

Characterization of PdNPs

The solution was monitored for the formation of PdNPs at different time intervals by an UV-vis spectrophotometer (Schimadzu UV-1800). Fourier Transform Infrared Spectra (FTIR) was carried out by KBr pellet method using Perkin Elmer Spectrum at a range of 4000 cm^{-1} to 450 cm^{-1} before and after the reduction reaction. Transmission Electron Microscopy (TEM) analysis was studied to findout the size and morphology of the PdNPs. It was done by drop coating the PdNPs onto a carbon coated TEM grid, air dried and the images were photographed using a JEOL 3010. X-ray diffraction (XRD) pattern of PdNPs was obtained using Rigaku smart lab instrument operated at a voltage of 40 kV and a current of 30 mA with CuK_{α} radiations.

RESULTS AND DISCUSSION

The detailed experimental study reveals that a mixture of $PdCl_2$ and plant extract in the ratio 80:20 shows complete bioreduction of Pd (II) ions when subjected to pH 3 at room temperature for 64 h. The complete bioreduction was evident from the colour change straw yellow to brownish yellow[17]. The UV-vis absorption spectra were recorded before (Fig 1) and after the bioreduction (Fig 2). Initially, intense peaks were observed in a wavelength range of 250–400 nm. On complete bioreduction, the PdNPs shows the maximum excitation at 302 nm which is due to the surface plasmon vibrations of PdNPs (Fig 2). On reduction, the peak around 380 nm has shifted to a lower wavelength of 302 nm which

can be assigned to the presence of PdNPs[18,19].

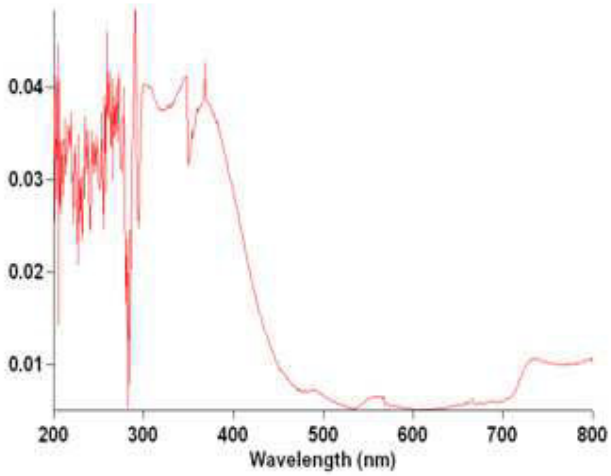

Figure 1
UV-vis spectra of aqueous leaf extracts of Coleus amboinicus

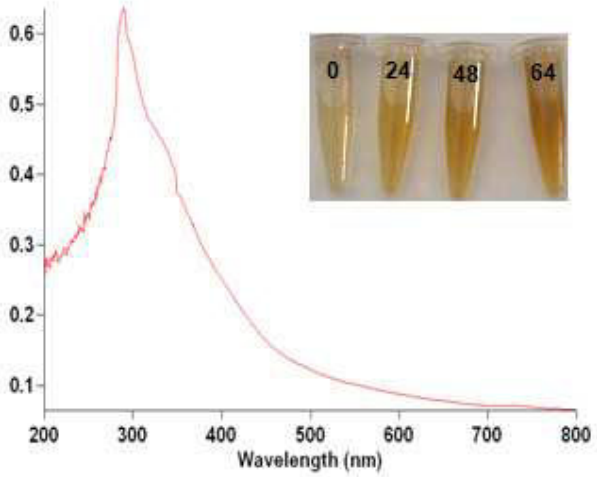

Figure 2
UV-vis spectra of PdNPs (A) Inset shows colour changes and formation of PdNPs at different time intervals (0, 24, 48, 64 h).

The IR spectra of the system were compared in order to find out the bioreduction before and after based on the point of attachment. The IR spectra showed a strong absorption at around 3401 cm^{-1} - 3423 cm^{-1} confirms the presence of –OH group[20]. The absorption band at 1644 cm^{-1} has shifted to 1650 cm^{-1} which shows the presence of amide (C=O) group has involved in the formation of PdNPs. The peak at 1393 cm^{-1} is due to C-N stretch for encapsulation of PdNPs[21]. The results of FTIR spectra, confirms the bioreduction of hydroxyl group of sugar and amide to a carbonyl group.

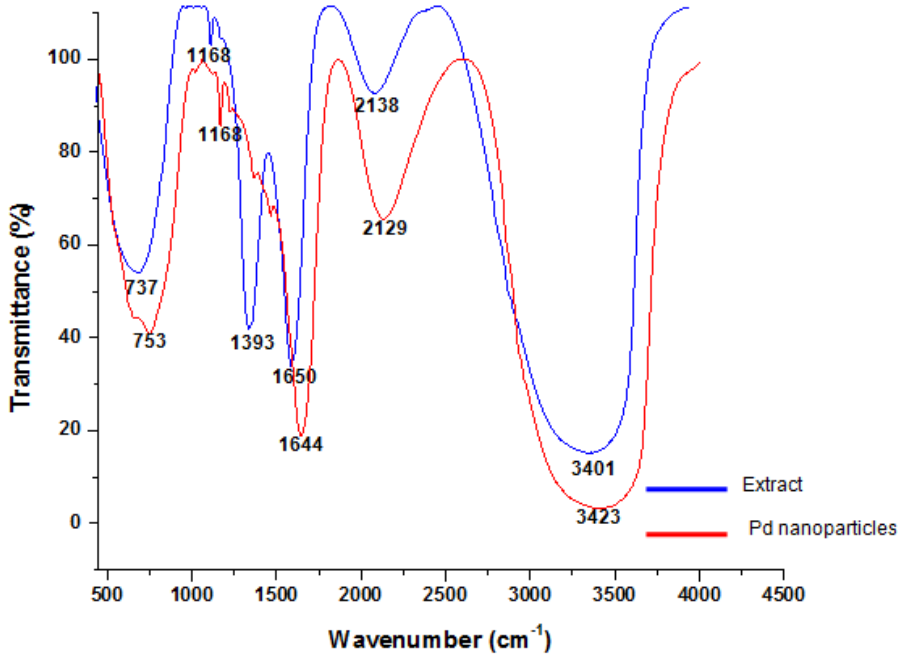

Figure 3
FT-IR spectra of the extract and synthesized PdNPs

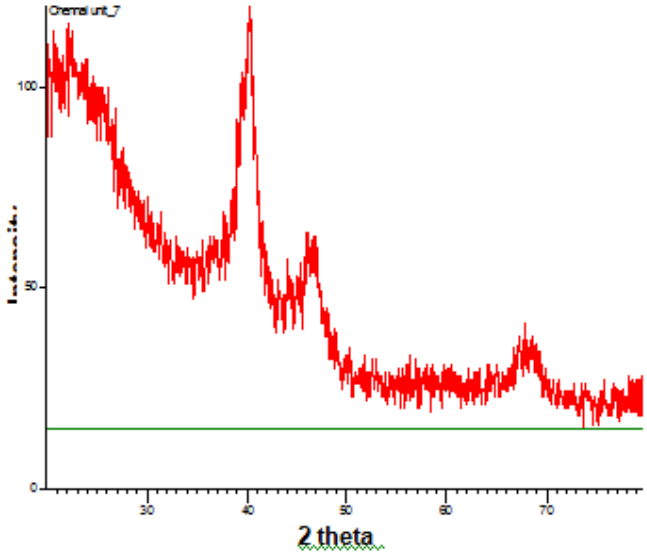

Figure 4
XRD patterns of the PdNPs synthesized using aqueous leaf extract of C. amboinicus.

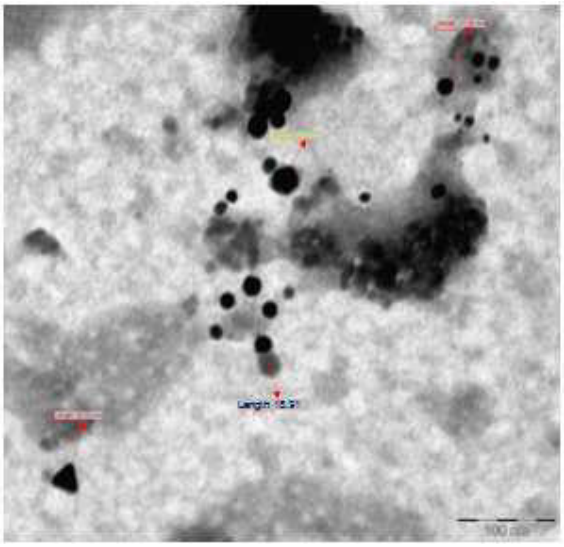

Figure 5
TEM image of PdNPs showing polydisperse (spherical, Triangular and pentagon) shaped particles.

The TEM image shows PdNPs of different shapes (spheres, triangle and pentagon) distribution in the ranged from 10 to 28 nm with a ca. 19 nm in diameter (Fig 5). In XRD studies the crystalline nature of the PdNPs was analysed and the pattern were observed. XRD pattern (Fig 4) shows intense peaks at 2θ in the range of 30-70º which can be indexed as (111), (200) and (220) reflections of the fcc structure of metallic palladium revealing that the synthesized PdNPs are composed of pure crystalline palladium. The particle size of PdNPs calculated using Debye–Scherrer equation was found to be around 20 nm which are in agreement with the TEM results[22]. The result obtained was found to be consistent with the earlier reports on the XRD pattern of PdNP[23]. It is believed that the synthesized PdNPs will have the potential usage of catalytic activity in chemical and biological reactions.

CONCLUSION

In the present work, *in situ* green approach for the synthesis of palladium nanoparticles from the potential herb *C. amboinicus* has been carried out. The complete bioreduction of Pd (II) ions was achieved at pH 3 at room temperature in 64 h, and it was confirmed by using UV-Vis, IR, XRD and TEM. The PdNPs formed polydisperse with particle size ranging from 10-28 nm. This method can be scaled up easily for commercial production of PdNPs for various industrial applications.

REFERENCES

1. Kim SW, Park J, Jang Y, Chung Y, Hwang S, Hyeon T, Synthesis of Monodisperse Palladium Nanoparticles. Nano Letters, 3 (9): 1289–1291, (2003).
2. Moreno-Manas M, Pleixats R, Formation of Carbon-Carbon Bonds Under Catalysis By Transition-Metal Nanoparticles. Acc. Chem. Research, 36 (8): 638–643, (2003).
3. Chen S, Ostrom C, Chen A, Functionalization of TiO_2 Nanotubes with Palladium Nanoparticles for Hydrogen Sorption and Storage. Int. J. Hydr. Energy, 38 (32): 14002-14009, (2013).
4. Li Z, Zhang J, Zhou Y, Shuang S, Dong C, Choi MMF, Electrodeposition of Palladium Nanoparticles on Fullerene Modified Glassy Carbon Electrode for Methane Sensing. Electrochim. Acta, 76 (1): 288–291, (2012).
5. Collins G, O'Dwyer C, Morris M, Holmes JD, Palladium Catalyzed Coupling Reactions For The Functionalization of Si Surfaces: Superior Stability of Alkenyl

Monolayers. Langmuir, 29 (38): 11950–11958, (2013).
6. Jia L, Zhang Q, Li Q, Song H, The Biosynthesis of Palladium Nanoparticles by Antioxidants In *Gardenia jasminoides* Ellis: Long Lifetime Nanocatalysts For P-Nitrotoluene Hydrogenation. Nanotechnology, 20 (38): 385601, (2009).
7. Zhang H, Jin M, Xiong Y, Lim B, Xia Y, Shape-Controlled Synthesis of Pd Nanocrystals and Their Catalytic Applications. Acc. Chem. Res, 46 (8): 1783–1794, (2013).
8. Govindaraju K, Khaleel Basha S, Ganesh Kumar V, Singaravelu G. Silver, gold and bimetallic nanoparticles production using single-cell protein (Spirulina platensis) Geitler. J.Mater. Sci, 43 (15):5115-5122, (2008).
9. Dhas TS, Kumar VG, Karthick V, Angel KJ, Govindaraju K, Facile Synthesis of Silver Chloride Nanoparticles Using Marine Alga And Its Antibacterial Efficacy. Spectrochim. Acta A, 120 (24): 416–420, (2014).
10. Rajathi FAA, Parthiban C, Kumar VG, Anantharaman P, Biosynthesis of Antibacterial Gold Nanoparticles Using Brown Alga, *Stoechospermum marginatum* (kützing). Spectrochim. Acta A, 99 (15): 166–173, (2012).
11. Dauthal P, Mukhopadhyay M, Biosynthesis of Palladium Nanoparticles Using Delonix regia Leaf Extract and Its Catalytic Activity for Nitro-aromatics Hydrogenation. Ind. Eng. Chem. Res, 52 (51): 18131–18139, (2013).
12. Jia L, Zhang Q, Li Q, Song H, The Biosynthesis of Palladium Nanoparticles By Antioxidants In Gardenia Jasminoides Ellis: Long Lifetime Nanocatalysts for P-Nitrotoluene Hydrogenation. Nanotechnol, 20 (38) 385601, (2009).
13. Abuga AN, Rosarioa RMD, Palmesa ND, Herbs and Spices, An Anticancer Potential, International Journal of Science and Nature, 3(3), 491-496, (2012).
14. Khare CP, Indian Medicinal Plants: an Illustrated Dictionary Library of Congress Control Number: 2007922446 ISBN: 978-0-387-70637-5 Springer-Verlag Berlin Heidelberg, Springer science+ Business Media, LLC (2007).
15. Cano JH, Volpato G, Herbal Mixtures In The Traditional Medicine of Eastern Cuba. Journal of Ethnopharmacology, 90 (2-3): 293–316, (2004).
16. Langenberger G, Prigge V, Martin K, Belonias B, Sauerborn, Ethnobotanical Knowledge of Philippine Lowland Farmers And Its Application In Agroforestry. J. Agroforest Syst, 76: 173-194, (2009).
17. Kim SW, Park J, Jang Y, Chung Y, Hwang S, Hyeon T, Synthesis of Monodisperse Palladium Nanoparticles. Nano Letters, 3 (9): 1289–1291, (2003).
18. Hamasaki A, Yasutake Y, Norio T, Ishida T, Akita T, Ohashi H, Yokoyama T, Honma T, Tokunaga M, Cooperative Catalysis Of Palladium Nanoparticles And Cobalt Oxide Support For Formylation Of Aryl Iodides Under Syngas Atmosphere. Appl. Catalysis A: General, 469 (17): 146-152, (2014).
19. Huang J, Li Q, Sun D, Lu Y, Su Y, Yang X, Wang H, Wang Y, Shao W, He N, Hong J, Chen C, Biosynthesis Of Silver And Gold Nanoparticles By Novel Sundried *Cinnamomum camphora* Leaf . Nanotechnol, 18: 105104-105114, (2007).
20. Dhas TS, Kumar VG, Abraham LS, Karthick V, Govindaraju K, *Sargassum myriocystum* Mediated Biosynthesis of Gold Nanoparticles. Spectrochim. Acta A, 99 (15): 97–101, (2012).
21. Govindaraju K, Kiruthiga V, Ganesh Kumar V, Singaravelu G. Extracellular synthesis of silver nanoparticles by a marine alga, *Sargassum wightii* Grevilli and their antibacterial effects. J. Nanosci. Nanotechnol. 9: 5497–5501, (2009)
22. Kumar KM, Mandal BK, Kumar KS, Reddy PS, Sreedhar B, Biobased Green Method To Synthesise Palladium And Iron Nanoparticles Using *Terminalia chebula* Aqueous Extract Spectrochim. Acta A, 102:128–133, (2013).
23. Dauthal P, Mukhopadhyay M, Biosynthesis of Palladium Nanoparticles Using *Delonix regia* Leaf Extract and Its Catalytic Activity for Nitro-aromatics Hydrogenation. Ind. Eng. Chem. Res, 52 (51): 18131–18139, (2013).