Ultrasonication for Fabrication of Palladium Nanoparticles using Andean Mora fruit

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***Abstract*— In this investigation, we report a rapid and eco-friendly method for the fabrication of palladium nanoparticles (PdNPs) using Andean Mora fruit extract, as a bioreductant and ultrasonication. The fabricated PdNPs were characterized using visual, UV-vis-NIR spectroscopy, transmission electron microscopy (TEM), Dynamic Light Scattering (DLS) and X-ray diffraction (XRD). TEM, DLS and XRD analysis confirmed PdNPs are spherical, 50-70 nm and crystalline face-centered cubic structure. Furthermore, the as-fabricated PdNPs demonstrated weak antioxidant activity (>8%, 0.05 mM) against 1,1-diphenyl-2-picrylhydrazyl and strong photocatalytic degradation towards the methylene blue (>77%, 10 mg/L), efficiently. Ultrasonication enhanced biofabrication of nanomaterials finds the edge over chemical methods due to its economical and environmental compatibility.**

Keywords—Palladium nanoparticles; Andean Mora; TEM; XRD; Antioxidant; Photocatalyst

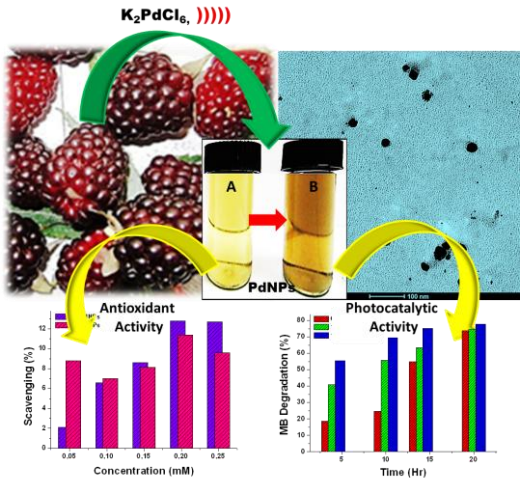
I. INTRODUCTION

In the last few decades, palladium nanoparticles (PdNPs) are taken with immense interest by researchers from diverse fields due to their application as a catalyst [1], sensors [2], membrane materials [3] etc. In general, nanostructured materials have one spatial dimension in the range of 1–100 nm consisting of nanoscale structures e.g. nanorods, nanowires and nanoparticles [4]. Many methodologies have been used to date, such as sol–gel [5], solution-based methods, chemical precipitation [6], sonochemical [7], hydrothermal [8] and biological processes [9]. However, most are not ecofriendly due to high capital costs and the use of toxic chemicals. The advantages of PdNPs are the ease of preparation and cheaper than other precious metals (silver, gold and platinum). Although, there are some reports on the biofabrication of PdNPs using banana peel [10], *Pulicaria glutinosa* [11], *Terminalia chebula* fruit [12], *Anacardium occidentale* leaf [13], *Cinnamomum camphora* leaf [14] and soybean leaf [15] as bioreductants.

In addition, there are scarce of reports concerning biofabrication of PdNPs by plant or fruit extract and ultrasonication simultaneously, where the ultrasonication enhances the reducing and stabilizing ability of fruit extract. Ultrasonication is a physical treatment with frequency higher than 16 kHz and locally creates a strong shear force, high temperature, and free radicals, which change the structure and properties of organic materials [7]. An important example of such a fruit is the Andean Mora (*Rubus glaucus* Benth.). The dark-red color, juicy, and flavored fruit is consumed mainly Ecuador and Colombia as fresh, jam, juice, frozen pulp and to a minor extent, wines [16]. We hypothesized that ellagitannins and anthocyanins could be applied in the synthesis of PdNPs.

Methylene Blue (MB) is a heterocyclic, solid, odorless, dark green powder with the molecular formula $C_6H_{18}N_3SCl$ and gives a blue solution in aqueous medium. It has applications in textile industry, analytical chemistry, electro optic devices, oxygen detecting and time monitoring. Its harmful effects on a living organism can cause vomiting, diarrhea and nausea [17].

In continuation of our ongoing research on the synthesis of different metal nanoparticles [7, 16-19], herein we report the use of Andean Mora fruit extract for the fabrication of PdNPs under ultrasonication. The present study is summarized in the Scheme 1. The extract of Andean Mora fruit (polyphenolic and flavonoidic groups) was first used to fabricate PdNPs in presence of ultrasonic irradiation. Spherical PdNPs were obtained and further characterized by UV–vis-NIR, TEM, DLS and XRD instrumental techniques. Further, the antioxidant and photocatalytic activity of the PdNPs was investigated by using 1, 1-diphenyl-2- picrylhydrazyl (DPPH) and MB.



Scheme 1

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II. MATERIALS AND METHODS

A. *Synthesis of PdNPs*

Potassium hexachloropalladate (IV), K_2PdCl_6, 99.998% and DPPH, >99.5% was purchased from Aldrich, USA. MB, 99.5 % was purchased from the Spectrum, USA. The extraction of the phytochemicals from Andean Mora fruits was performed by earlier method [16]. The collected fresh Mora fruit (5 g) was washed thoroughly and heated (65-70°C) in 50 mL of deionized water for 60 min. After cooling, pinkish-red color extract was filtered using Whatman paper no.1. For green synthesis, 1.0 mL of Mora fruit extract was mixed with 10 mL, 1 mM K_2PdCl_6 solution and kept at 25 °C for 24 hours then perform ultrasonication for 30 mins [7]. Fabrication of PdNPs was confirmed by the change of yellowish reaction mixture to yellowish-black.

B. *Radical scavenging activity*

The scavenging activity of the PdNPs was measured by using DPPH as a free radical model and a method adapted from Kumar *et al*., 2014 [19] with slight modifications. An aliquot (1000-200 μL) of PdNPs or control and (1000-1800 μL) of H_2O was mixed with 2.0 mL of 20 μM (DPPH) in ethanol (95%). The mixture was shaken vigorously and allowed to stand at room temperature for 30 min in the dark. Absorbance of the mixture was measured spectrophotometrically at 517 nm, and the free radical scavenging activity was calculated using Eq. (1):

$$\text{Scavenging effect (\%)} = [1 - \{\text{absorbance of sample}/\text{absorbance of control}\}] \times 100 \quad (1)$$

The scavenging percentage of all samples were plotted. The final result was expressed as % of DPPH free radical scavenging activity (mM).

C. *Decomposition of MB study*

The photocatalytic activity of the PdNPs was measured by Kumar et al., 2014 [17] method. Four separate sets of experiments were performed to study the decomposition of MB in visible light (55-60 Cd/ m^2), 20-25 °C. In set 1, 5 mL MB (10 mg/L) kept in a vial in visible light. In set 2, 3 and 4, the synthesized PdNPs were used; 5 mL MB and 0.5, 1.0 and 1.5 mL PdNPs were mixed and kept in visible light without stirring. All four sets of reaction were observed after 4, 10, 14 and 20 hrs. The rate of MB dye decomposition was monitored by taking 4 mL samples from each set and recording the absorbance measurements at the λ_{max} = 664 nm, before and after degradation. The average decomposition in terms of the percentage of MB in solution was calculated using the following equation (2):

$$\eta = [1 - At/Ao] \times 100\% \quad (2)$$

where η is the rate of decomposition of MB in terms of percentage, Ao is the initial absorbance of MB solution and At is the absorbance of the MB at time t [19].

D. *Characterization of PdNPs*

The synthesized PdNps was characterized with the help of a UV-visible, single beam spectrophotometer (Thermo Spectronic, GENESYS^{TM} 8, England). Transmission Electron Microscopy (TEM) and selected area electron diffraction (SAED) were recorded digitally (FEI Tecnai G2 spirit twin). The hydrodynamic size distributions of nanoparticles were analyzed by using Dynamic Light Scattering (DLS) instrument (HORIBA LB -550). X-ray diffraction (XRD) studies on thin films of the nanoparticle were carried out using a PANalytical brand θ-2θ configuration (generator-detector) x-ray tube copper λ = 1.54 A° and EMPYREAN diffractometer.

III. RESULTS AND DISCUSSION

A. *Visual and UV-vis-NIR study*

Fig. 1 and 2 shows the visual and UV-vis-NIR studies of PdNPs for 24 hours at room temperature and after ultrasonication. The visual color change of reaction mixture from yellow to yellowish-black color, clearly indicates the reduction of Pd^{2+} to Pd and formation of PdNPs (Fig. 1a, b), which is enhanced by ultrasonication [11]. In Fig. 2, UV-vis absorption spectra for Mora fruit extract at λ_{max} = 480-550 nm, starts disappearing and new spectra appears with the progress of time. It clearly indicates the involvement of phytochemicals of Mora fruit in the biofabrication of PdNPs. After ultrasonication, a broad continuous absorption was observed (300-700 nm) indicating complete reduction of Pd^{2+} to PdNPs and suggests the surface plasmon of PdNPs [12, 13].Thus, UV–vis-NIR spectroscopy is a suitable method for initial prediction of PdNPs formation.

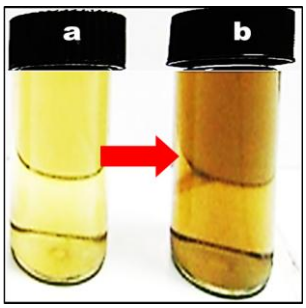

Fig. 1. Reaction mixture (a) before and (b) after ultrasonication

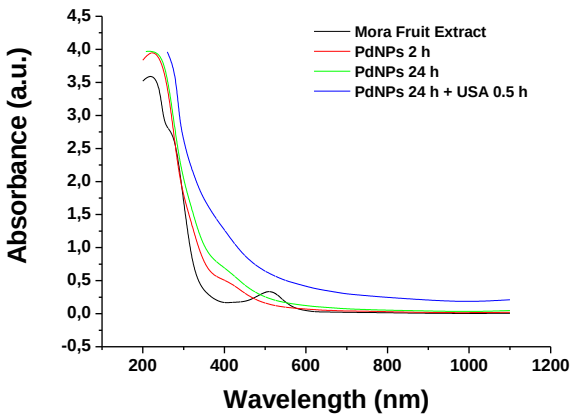

Fig. 2. UV-vis-NIR spectrum of PdNPs

B. TEM-SAED and DLS study

TEM images, SAED patterns and average particle size by DLS of PdNPs prepared by ultrasonication are depicted in Fig. 3. Fig. 3 (a, b) clearly illustrates as-prepared PdNPs are spherical, well dispersed and average size in the range of 50-70 nm. The measurement of the size was performed along the largest diameter of the particles. The SAED patterns of PdNPs (Fig. 3c) recorded from the spherical Pd nanostructures and it clearly shows the ring like electron diffraction patterns, typical of polycrystalline PdNPs. The average particle size distribution of PdNPs is 66.7±34.4 nm (Fig. 3d) and it is in agreement with the results of TEM images.

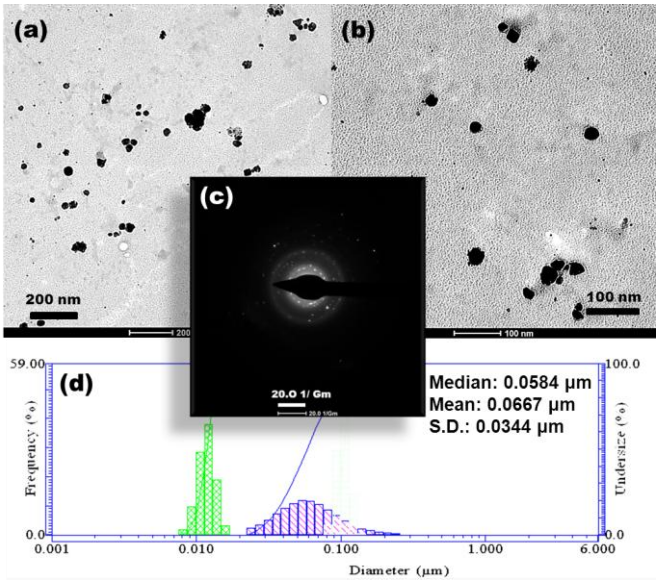

Fig. 3. TEM images (a-b), SAED pattern (c) and DLS (d) micrograph of PdNPs

C. XRD study

The XRD patterns of thin films of the PdNPs prepared by ultrasonication are shown in Fig. 4. Four intense peaks were observed at 39.9°, 44.8°, 67.9°, 81.2° (ICSD No. 98-0006-4920) due to (1 1 1), (200), (220) and (311) planes of face centered cubic (fcc) lattice of palladium, respectively [11-13]. The predominant orientation of Pd nanocrystals is along (111) plane, as the most intense peak corresponds to the same.

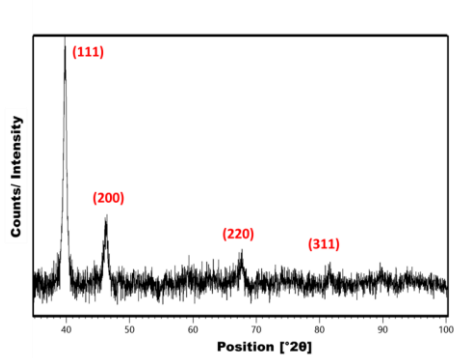

Fig. 4. XRD pattern of PdNPs

D. Antioxidant Activity

The antioxidant activity of the PdNPs was estimated by comparing the % inhibition of DPPH radicals (Fig. 5). The DPPH radical scavenging activity of PdNPs prepared at room temperature increases with increasing concentration (0.05 mM–2.1%; 0.1 mM–6.6 %; 0.15 mM–8.62%, 0.2 mM-12.79 and 0.25 mM–12.7%) whereas dramatic changes occurred with PdNPs by ultrasonication, (0.05 mM–8.81%; 0.1 mM–7.01 %; 0.15 mM–8.15% , 0.2 mM-11.37 and 0.25 mM–9.57%). At low concentration, PdNPs prepared by ultrasonication method exhibited stronger antioxidant activity than room temperature method. The antioxidant effects of the PdNPs might be the result of an active physicochemical interaction of Pd atoms with the functional groups of the Mora fruit extract [16, 19].

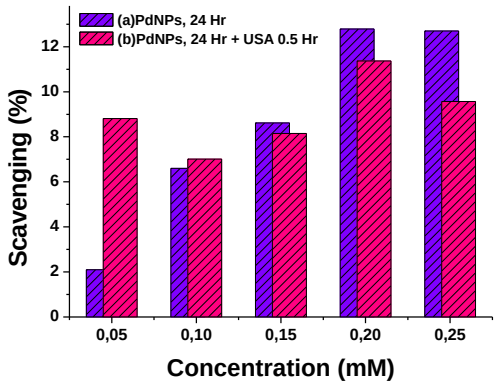

Fig. 5. DPPH assay of PdNPs (a) 24 hr room temperature and (b) ultrasonication

E. Photocatalytic activity

The photocatalytic activity of the PdNPs for the degradation of MB (10 mg/L, 5 mL) under visible light was found satisfactory (Fig. 6). Initially, the degradation of MB is slow and photodegradation capacity increases with an increase in the amount of Pd nanocatalyst (0.5-1.5 mL). Initial degradation of MB for 4 hrs was found to be 18.72%, 41.01% and 55.41% with the addition of 0.5, 1.0 and 1.5 mL of PdNPs in visible light.

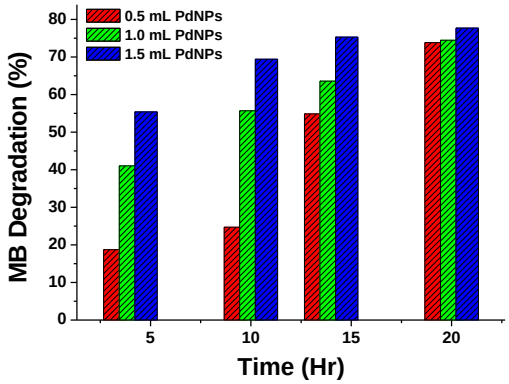

Fig. 6. Photocatalytic degradation of MB using PdNPs in visible light

The degradation activity of MB is increased with time and saturated with 73.82%, 74.45% and 77.7% for 20 h. It clearly indicates that higher surface area of nanocatalyst enhanced the degradation of MB. In the valence band (VB), the holes interact with water molecules, resulting in the formation of hydroxyl radical (·OH) and proton. We hypothesized that, PdNPs act as an electron transfer mediator between the proton and MB by acting as a redox catalyst via electron relay effect [17]. These protons are responsible for the degradation of MB molecules.

IV. CONCLUSION

We have demonstrated an ultrasonication approach for the fabrication of PdNPs using Andean Mora fruit as an effective bioreductant. Applying this method, spherical shaped, 50-70 nm size and crystalline PdNPs were prepared without using any toxic or hazardous chemicals. The as-prepared PdNPs exhibited weak antioxidant activity (>8%, 0.05 mM) against 1, 1-diphenyl-2-picrylhydrazyl and strong photocatalytic degradation towards the methylene blue (>77%, 10 mg/L). Therefore, the mentioned protocol is economical, ecofriendly and can easily be exploited for the large-scale fabrication of PdNPs.

ACKNOWLEDGMENT

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