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Catalytic efficiency of green synthesized palladium nanoparticles by *Sterculia acuminata* extract towards abatement of organic pollutants

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ABSTRACT

The catalytic efficiency of biogenic palladium nanoparticles (PdNPs) using *Sterculia acuminata* (*S. acuminata*) seed extract has been verified towards organic pollutants in this report. The extract has played a vital role as multifunctional agent. The synthesized PdNPs were examined using UV–Vis absorbance spectrophotometer, XRD, Transmission electron microscope (TEM), FT-IR, Average particle size with potential studies. Further, HPLC was used to know the available compounds present in the *S. acuminate* seed extract. Transmission electron microscopy and PSA analysis showed an average particle size of PdNPs as ~26.5 nm. The FCC crystallinity of PdNPs was determined by diffraction analysis and was confirmed with TEM-SAED pattern. FT-IR analysis demonstrates the presence of functional groups in *S. acuminata* seed extract and PdNPs surface. These PdNPs also act as excellent catalyst in the reduction of p-Nitrophenol (p-NP) to p-Aminophenol (p-AP) in the existence of $NaBH_4$.

Keywords: *Sterculia acuminate; 4-Nitrophenol; palladium nanoparticles; 4-aminophenol; catalytic activity.*

1. INTRODUCTION

In recent years nanoparticles (NPs) are widely used in the fabrication of advanced materials, supercomputers, energy storage devices, drug delivery, optical displays and biomedical devices [1]. Based on the size and shape metals nanoparticles exhibit some distinct futures. Among these noble metals, preparation of Pd NPs has high lightened because of their high catalytic performance in various homogeneous and heterogeneous reactions [2]. Pd NPs have been used in various oxidation reactions, hydrogenation, electrochemical reactions in fuel cells and carbon–carbon bond formation [3-5]. For that reason, synthesis of well-defined Pd NPs with different sizes, shapes and morphology have been confirmed through various physical and chemical methods such as thermal decomposition [6], ion exchange [7], electrochemical and chemical reduction [8], vapor deposition and polyol method [9]. But, these conventional methods are associated with adverse effects on human and environmental costs, due to the use of toxic solvents and reducing agents [10]. Recent days, huge efforts have been made toward synthesizing of these NPs using green methods. Biogenic methods are advantageous over other conventional methods because of their cost, simplicity and time efficient. Plant mediated NPs are more favored option for a variety of applications because of eco-friendly nature and stability [11].

Very few reports are accessible on the green synthesis mediated Pd NPs when compared to green synthesis of gold and silver nanoparticles, some of the plant species used are *Anacardium occidentale* [12] *Cinnamon zeylanicum* [13], *terminalia chebula* [14,15], *Hippohae rhamoides* [16], *Punica granatum* [17], *Ocimum sanctum* [18], coffee arabica fruit [19] and Sterculia acuminata fruit [20-22]. Since PdNPs are known for their catalytic efficiency, use of these plants mediated nanoparticles as a catalyst is rare for the degradation and conversion of risky water waste. p- Nitrophenol (p-NP or 4-NP) is one such toxic component which is dangerous to the environment and human health due to its carcinogenic properties [23-27]. 4-NP has been widely used as raw materials in various industries such as pharmaceutical, preparation of insecticides and dyes [28-30]. Hence it is essential to demolish the presence of 4-NP from industrial and agricultural wastewater.

The present study involves plant mediated of PdNPs using seed extract of *Sterculia acuminata (S. acuminata)*, it contains minute percentile of catechine-caffeine (colanine), which have a great level of alkaloids leading to pharmaceutical uses in Africa. This work reveals the easy way to synthesize stable PdNPs. Synthesized PdNPs is characterized using different characterization techniques. Further, the catalytic efficiency of PdNPs is used as catalyst in reducing 4-NP under room to 4-AP with the kinetic study.

2. EXPERIMENTAL SECTION

2.1. Material preparation.

Palladium dichloride ($PdCl_2$), sodium borohydride ($NaBH_4$) and 4-Nitro phenol were bought from S.A., India. *S. acuminata* seeds were gathered from VIT University Vellore, India.

2.2. Preparation of *Sterculia acuminata* (*S. acuminata*) *seed* extract.

Sterculia acuminata (S. acuminata) fruits pericarp was removed, dried under Sun light and stored. For the preparation of *S. acuminata* seed extract, 35 mg of stored seed powder was

suspended in 110 mL of double distilled water, put in water-bath at ~87 ^{0}C for 25 min. Furthermore, *S. acuminata* seed extract was filtered by 0.44 µm filter. The pH of extract was ~3.7 without using any external acid/base.

2.3. Preparation of catalyst (palladium nanoparticles, PdNPs) using *S. acuminata* seed extract.

50 mL Palladium dichloride ($PdCl_2$) (0.01M) (pH=3) was mixed with 250 mL *S. acuminata* seed extract (1:5). Here, reflection method (using magnetic heater and condenser) is used for the preparation of PdNPs. Continuously, development of PdNPs with color change was noticed by naked eye from pale yellow to black, which indicated the development of PdNPs (within 30 min) and further which was proved by spectrophotometric analysis.

2.4. Characterization.

2.4.1. UV-vis absorbance spectroscopy. The absorbance studies of synthesized PdNPs were confirmed by Jasco V-670 UV-Vis spectrophotometer with 8 times suspension of PdNPs. The absorbance was noted from 200- 800 nm and these results were re-plotted using Origin Pro 8.0 software. After the formation of PdNPs, nanoparticles were detached by centrifugation at 6500 rpm for 0.5 h. Initially supernatant of the solution was used for HPLC analysis and obtained solution washed with water and ethanol, then dries and subjected to auxiliary studies.

2.4.2. XRD studies. To identify the phase and crystallinity of PdNPs XRD analysis was done by Bruker D8 advance diffractometer and spectra were noted ranging from 10^0 to 90^0 (scanning rate: 4^0/min, step size : 0.02^0).

2.4.3. HR-TEM studies. To determine the size, shape and crystallinity of PdNPs, transmission electron microscopy and SAED analysis were performed by JEOL-JEM 2100 HRTEM (voltage: 200 kilo V). 400 µL of PdNPs suspension was dispersed by adding 2 mL distilled water and then sonicated and further this sample solution was drop casted onto the Cu-grids, further permitted to evaporate under room temperature.

2.4.4. Dynamic light scattering and zeta potential studies. To know the average size and stability of PdNPs dynamic light scattering (DLS) and zeta potential measurement were performed by Horiba scientific nanoparticle analyzer (nanoparticci, SZ-100).

2.4.5. FTIR studies. Responsibility of functional groups in multifunctional nature (reducing and stabilizing) of seed extract was identified using FTIR (Shimadzu IR AFFINITY-1) studies of PdNPs. Herein spectrum of *S. acuminata* seed powder was used as reference.

2.4.6. HPLC studies. To determine what are the secondary metabolites existed in *S. acuminata* seed extract HPLC studies were performed by using Perkin Elmer 200 Series high performance liquid chromatography furnished with UV–Visible detector under gradient conditions.

2.5. Catalytic studies.

Catalytic study of PdNPs was done by reducing 4-NP to 4-AP. Initially, $NaBH_4$ was added to the 4-NP containing tube in the absence of PdNPs. Initially, the intermediate forms of 4-NP i.e. 4-Nitorphenolate ion was formed and then further the reduction of 4-Nitorphenolate ion to 4-Aminophenal (4-AP) was done by varying the concentrations of PdNPs (5µg to 50µg per mL) to 4-Nitrophenolate ion solution. The catalytic reduction of 4-NP was monitored and spectra were recorded using absorbance spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Catalyst synthesis and its characterization.

Initially different ratios of extract to $PdCl_2$ were attempted to synthesize PdNPs but the development of any color change was not noticed with the naked eye at mild conditions. When the reactions were carried out at 60 °C, the reaction mixture turned black in 30 min with the 1: 5 ratio of $PdCl_2$: seed extract indicating the formation of PdNPs. From this study, it is clear that higher reaction temperature is essential for the conversion of Pd ions to Pd NPs (Pd bulk to Pd nano form) which may be due to lower reduction potential. Effect of pH on the development of PdNPs was also examined by varying the pH (2-10) of the reaction medium at 60 ^{0}C. At pH < 3 the reaction did not progress while the formation of PdNPs was observed in between 4≤ pH≥7 and as the pH increased the time required for the development of Pd NPs was also increased. At pH≥8 agglomeration was absorbed leading to the formation of larger size NPs. The different parameters optimized for synthesizing PdNPs required for the further studies in the present work were 1:5 ratios of 0.01 $PdCl_2$ and 1g/250 mL *S. acuminata* seed extract and different pH solution under mild conditions. Development of PdNPs was noticed through visual color change in the solution and then further was confirmed by UV-Visible study (Fig. 1).

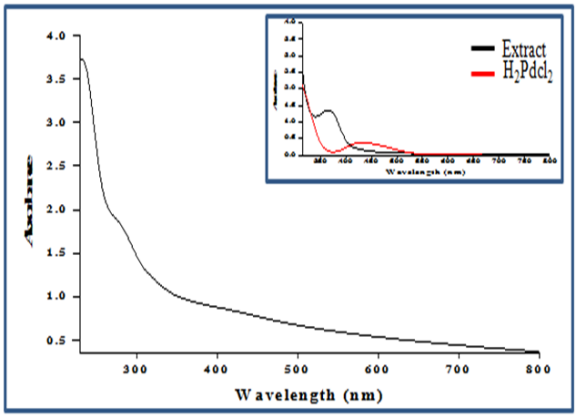

Figure 1. UV-Vis absorbance spectra of PdNPs (inset: H_2PdCl_2 and *S. acuminata* seed extract).

Crystal phase and structure of PdNPs were established by XRD analysis. The intense peaks of PdNPs appeared at 2θ values of 40.15^0, 46.62^0, 68.01^0, 82.12^0 and 86.64^0 corresponding to (111), (200), (220), (311) and (222) crystal reflection planes. This FCC crystallinity of PdNPs (JCPDS No. 96-900-2958) is explained from Fig. 2 and the crystallite/grain size of PdNPs is calculated using well known Scherrer's equation as, [$D = 0.9\lambda/\beta\cos\theta$], where D is the crystallite size, λ is the X-ray wavelength, k is a dimensionless shape factor, β is the line

broadening at half the maximum intensity (FWHM), and θ is the Bragg angle. From this calculation avg. the grain size of PdNPs is ~25.7 nm.

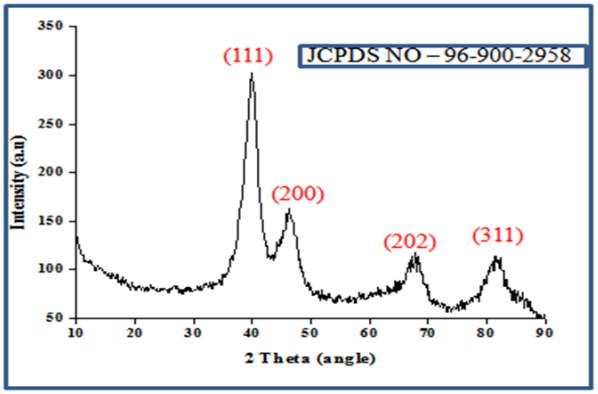

Figure 2. XRD pattern of PdNPs synthesized by using *S. acuminata* seed aqueous extract.

The average size of PdNPs is within 9 - 27.5 nm (Fig.3A, B and C) with the majority of spherical shapes. The synthesized spherical PdNPs were stable because the presence of polyphenols of extract stabilized PdNPs with the combination of carbonyl groups present in oxidized/quinine forms of polyphenols by capping on PdNPs surfaces. Because of fast reduction reaction at mild conditions, sintering/congregation, the undefended spherical PdNPs may lead to the growth of different shapes such as pentagonal, triangular etc. The spacing between the fringes is 2.263A ˚ (Fig. 3C) which confirms with a spacing of (111) Bragg's diffraction planes of face centered cubic PdNPs (JCPDS no. 96-900-2958). From the SAED studies, it reveals that the PdNPs were poly-crystalline and patterns were matched with XRD studies (Fig. 3D).

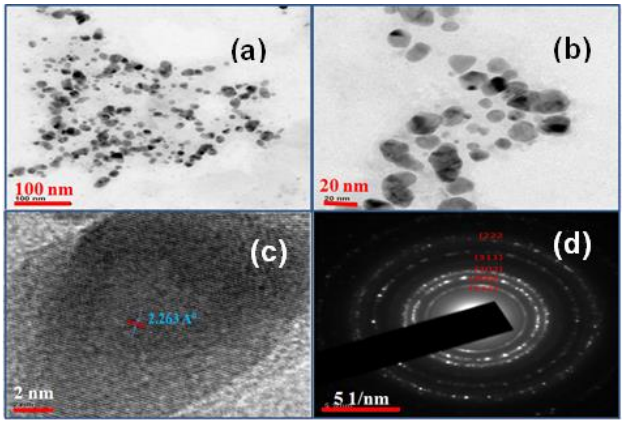

Figure 3. PdNPs at different magnifications: (A) 100 nm, (B) 20 nm, (C) 2 nm and (D) SAED pattern.

The particle size analysis (PSA) by DLS reveals average particles size of synthesized PdNPs as 26.5 nm (Fig. 4A) which is clear conformity with TEM reports and related zeta potential is -32.9 mV (Fig. 4B). These results are showing a good stability of PdNPs. The more negative potential might be due to the presence of biomass of *S. acuminata* seed extract on PdNPs surfaces.

FT-IR analysis (Fig. 5) of *S. acuminata* seed powder results in strong IR bands at 3257.19, 2327.52, 1609.93, 1316.61 and 1024.06 cm^{-1}. The IR bands noticed around 3257 and 2327 cm^{-1} correlate with –OH; aromatic –C-H stretching. The IR bands around 1024; 1316; 1609 cm^{-1} are due to –C–O; C–O–C; –C=O stretching.

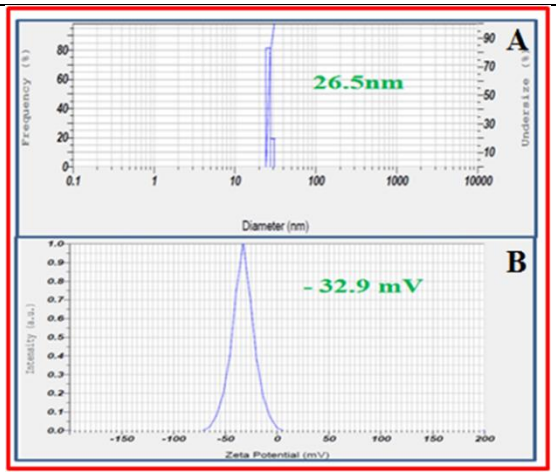

Figure 4. DLS analysis: Avg. nanoparticles size (A) and Zeta potential of PdNPs (B).

The IR bands of PdNPs result as a reduction of bands intensity compared to *S. acuminata* seed extract bands. This examination reveals the capping of secondary metabolites of *S. acuminata* seed extract onto the PdNPs. Furthermore, the PdNPs IR band intense peak around 1691 cm^{-1} is due to –C=O stretching, which confirms the prolonged stability of NPs with the presence of capping of oxidized/quinine forms of polyphenols.

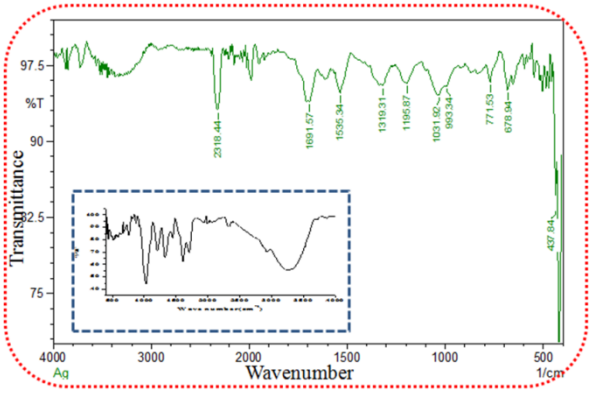

Figure 5. Fourier transform IR spectra of PdNPs and *S. acuminata* seed powder (inset).

3.2. Plausible mechanism for the formation of catalyst (Pd NPs).

HPLC chromatograms show that *S. acuminata* seed extract resembles majorly to ascorbic, gallic acids, pyrogallol and methyl gallate (Fig.6). These are water-soluble phytochemicals present in *S. acuminata* seed extract with 3-OH groups to its skeleton. In general, the molecules which are having at least 2-OHs at para locations were involved in the formation of nanoparticles [31]. The identified active components involved in the reduction from palladium to PdNPs and forms to the corresponding oxidized (or) quinine forms [32,33]. Moreover, those which is having at least 3 -OH groups, these are called as hard ligands. When these are near to the metal salt and associate with the Pd^{+2} ions, the reduction of Pd^{+2} to Pd^{0} (PdNPs) and at the same time all the polyphenols are converted into their respective oxidized/quinine forms. The carbonyl groups present in oxidized (or) quinine forms acts as soft ligands which favors synchronization onto PdNPs surfaces and ensures its stabilization (Fig. 7).

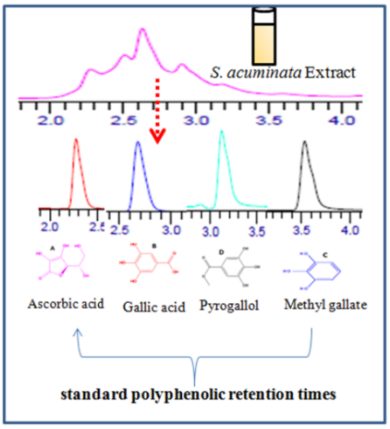

Figure 6. HPLC analysis of *S. acuminata* extract compared with standards

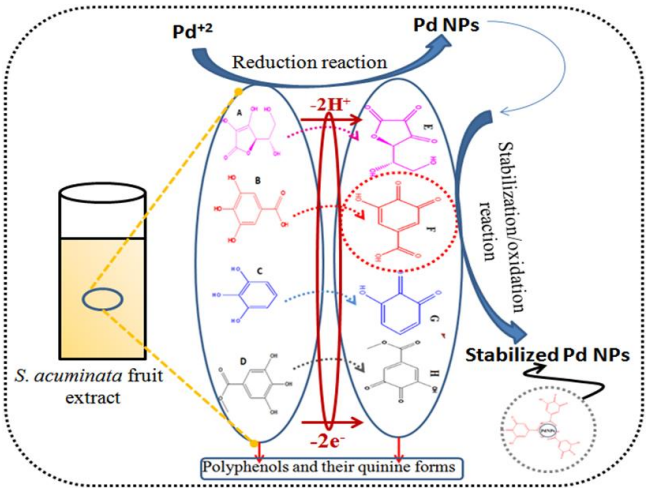

Figure 7. Plausible mechanism for reduction of 4-NP catalyzed by PdNPs.

HPLC analysis of *S. acuminata* seed extract was done to identify possible polyphenols i.e. plant secondary metabolites present in extracts, which participated in the reduction process (Pd^{+4} to Pd^{0} (Pd NPs)) followed by its stabilization. We analyzed the presence ofactive components in the *S. acuminata* seed extract using HPLC. In this report, *S. acuminata* seed extract exhibits several major peaks with retention times of 2.30, 2.61, 3.12 and 3.36 min. The obtained active components peaks matched with plant standard secondary metabolites such as ascorbic acid, gallic acid, pyrogallol and methyl gallate. The standard times for these active components were found at 2.28, 2.71, 3.17 and 3.57 min (Fig. 6). A small alteration in the retentions times was found when *S. acuminata* seed extract was injected and compared with standards because of matrices differs in *S. acuminata* seed extract compared to respective standards solution.

3.3. Catalytic activity

The catalytic performance of PdNPs was explored with decolonization of 4-NP in the presence of strong reducing agent $NaBH_4$. The aqueous 4-NP shows absorption peak around 316 nm (Fig. 8). Initially, accumulation of sodium borohydride to 4-nitrophenol was due to the development of 4-nitorphenolate ion which showed the absorption peak at 400 nm (Fig. 8).

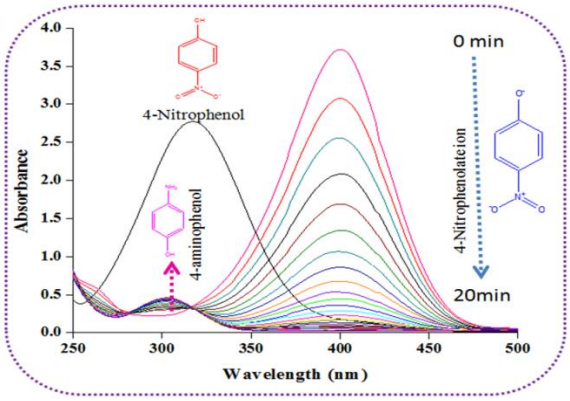

Figure 8. Catalytic efficiency of synthesized PdNPs towards reduction of 4-NP to 4-AP.

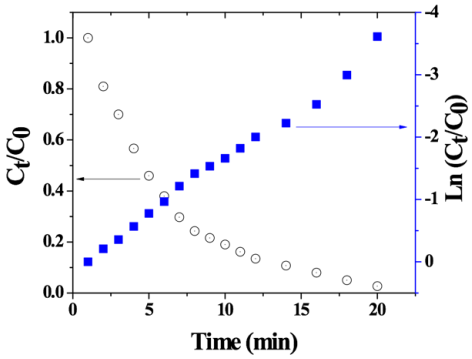

Figure 9. Kinetic study of 4-nitrophenol to 4-aminophenol using PdNPs as catalyst.

The probe reaction was not progressed without synthesized PdNPs. Interestingly, a new absorption peak around 295 nm appeared and slowly rose which indicated the formation of 4-aminophenol from 4-NP réduction (Fig. 8). Also, it showed the visual color difference from dark yellow colour to colour less. Since the quantity of reducing agent ($NaBH_4$) is very large, the elimination of 4-nitrophenol may correspond to well-known pseudo 1st order response (Fig. 8). From kinetics study, rate constant (k) is calculated as 0.179 min^{-1} and R^2=0.991 (Fig. 9).

4. CONCLUSIONS

In this investigation, the green one-pot and economical approach for the synthesis of PdNPs using *S. acuminata* seed extract is demonstrated. Formation of smaller size spherical PdNPs with the sizes less than 30 nm was evidenced by XRD, PSA and TEM analysis. The reduction and stabilization efficiency of *S. acuminata* seed extract mediated preparation proved multifunctional in the synthesis of PdNPs, which was well supported by HPLC and FTIR. Gallic acid present in *S. acuminata* seed extract as active component played the vital role in the formation of stable PdNPs. Based on this observation the plausible mechanism involved is presented for the formation of spherical PdNPs. These nanoparticles were used as a green catalyzing agent for the reduction of p-NP to p-AP using $NaBH_4$ as hydrogen donor. PdNPs exhibited effective catalytic efficiency and kinetics study showed pseudo 1st order kinetics. Hence this plant mediated route for the preparation of PdNPs is the best substitute to conventional methods and also provides a very smart way to synthesize toxic free metal NPs in large scale using renewable plant resources for different technological, environmental and medicinal utilization.

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