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Biosynthesis of Platinum Nanoparticles Using *Centella Asiatica* Aqueous Leaf Extract and Its Catalytic Activity in Reduction of 4-nitrophenol

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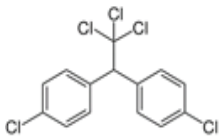
GRAPHICAL ABSTRACT



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ABSTRACT

Platinum nanoparticles (PtNPs) have been regarded as important catalyst in various organic reactions. In this research, a rapid and environmentally friendly method to prepare PtNPs using *Centella Asiatica* aqueous leaf extract is reported. The biomolecules found in *Centella Asiatica* aqueous leaf extract such as flavonoids are believed to act as reducing and capping agent. The formation of PtNPs is monitored by UV-Vis spectroscopy. The disappearance of a Pt(IV) ions absorption peak at 260 nm strongly suggested a complete reduction of Pt(IV) ions to Pt(0). The FTIR spectrum of PtNPs showed similar absorption bands with the spectrum of the *Centella Asiatica* leaf powder, suggesting the presence of biomolecules from as capping agent on PtNPs. HRTEM image analysis revealed that the PtNPs are mostly spherical with mean particle size of 10.62 nm ± 1.92. The catalytic activity of the biosynthesized PtNPs in the reduction of aqueous 4-nitrophenol to 4-aminophenol in the presence of sodium borohydride as reducing agent was also investigated. Results obtained showed the PtNPs is catalytically active achieving 86.6% conversion, follows a pseudo-first order reaction with rate constant value at 1.86×10^{-2} min^{-1}.

Keywords: Biosynthesis, platinum nanoparticles, Centella Asiatica, catalysis, 4-nitrophenol

1. INTRODUCTION

Nanotechnology has various benefits for the purpose of industrialized new materials at the nanoscale as it is one of the upcoming research fields in science and technology. Transition metal nanoparticles such as silver, gold, platinum and palladium have played important role in various field due to the uniqueness of their chemical and physical properties [10]. Nowadays, green syntheses of metal nanoparticles using leaf or microorganisms extract have attracted wide attention [3] as it is simple, low cost and more environmental friendly [3].

There are many conventional methods of synthesis metal nanoparticles including lithography, UV irradiation, and pyrolysis and chemical/photochemical/electrochemical synthesis[11]. However, chemicals techniques often required hazardous substances and conditions such as high temperature and pressure which can affect their nanoparticle uses [2]. Most commonly hazardous substances used in synthesis of metal nanoparticles are sodium borohydride, polyvinyl pyrrolidone (PVP) and tetradecylammonium bromide (TDAB). The uses of toxic materials on surface of nanoparticles limit their application in many fields thus it is become concern on using the toxic material. Physical technique required high temperature and pressure which consume high amount of energy even though it's free from uses of chemical toxicity [6]. Both chemical and physical methods of synthesis nanoparticles proved their efficiency to produce pure and well-defined metal nanoparticles; however clean and nontoxic methods for syntheses and assembly of metal nanoparticle must be developed to minimize or eliminate the use of energy and hazardous chemical or conditions. Therefore, biosynthesized of platinum nanoparticles (PtNPs) using *Centella asiatica* is been developed to synthesis platinum nanoparticles eco-friendly, cost effective and safe

The aim of this study is to apply *Centalla asiatica* as reducing agent to green synthesis of platinum nanoparticles. The progress of platinum nanoparticles synthesis was observed by UV-Vis Spectroscopy. The resulting product of PtNPs then is used as catalyst in reduction of 4-nitrophenol in aqueous solution in the presence of $NaBH_4$. The structural and morphological characterization of the biosynthesized PtNPs and *Centella asiatica* were determined by FTIR, and HRTEM.

2. EXPERIMENTAL

2.1. Materials

$H_2PtCl_6.6H_2O$, $NaBH_4$ and 4-nitrophenol are obtained from Sigma Aldrich. Deionized water is used throughout the process. Fresh leaves of *Centella Asiatica* are collected, thoroughly washed and air dried for 2 weeks and then finely powdered.

2.2. Synthesis of Platinum nanoparticles

The procedure of biosynthesis of PtNPs was followed previously reported method [4] with some modification. Chloroplatininc acid, H_2PtCl_6 was used as metal precursor. 100 mL of 1 mM of H_2PtCl_6 was prepared with deionized water. Then, 20 mL of leaf extract was placed in 50 mL round bottomed flask and 10 mL of 1 mM of H_2PtCl_6 was added into leaf extract solution with continuous stirring. After completion of the bio reduction, the Pt nanoparticles were collected by repeated centrifugation at 14800 rpm for 15 min and washed thrice with deionized water for characterization.

2.3 Characterization

In this study, UV-Vis Spectra was used to monitor progress of platinum nanoparticles biosynthesized. Then, Fourier-transform infrared spectroscopy (FTIR) was used to characterize *Centalla asiatica* extract and after synthesis of platinum nanoparticles. High Resolution Transmission Electron Microscope analysis (HRTEM) was used to determine the size and morphology of PtNPs and focusing on densely occupied Pt region.

2.4 Catalytic reduction of 4-nitrophenol

For 4-nitrophenol reduction, 2 mL of 0.1 mM of 4-nitrophenol is mixed with 3 mL of 0.1 M $NaBH_4$ is added with constant stirring. Then, 100 µL of Pt colloidal prepared is added to the solution. The change of color is observed in 120 minutes.

3. RESULTS AND DISCUSSION

3.1. UV-Visible Spectra

Figure 1 shows the UV-Visible spectra of the precursor $H_2PtCl_6.6H_2O$, leaf extract and the platinum colloids Figure 1 shows the UV visible spectra of the metal precursor, $H_2PtCl_6.6H_2O$ aqueous solution, the *Centella Asiatica* leaf extract and the produced PtNPs. The absorption peak value at 260 nm (Figure 1(a)) for the H_2PtCl_6 solution indicates the absorption of Pt(IV) ions due to strong metal ligand charge transfer transition between Pt(IV) and Cl^- ions [4]. Meanwhile, the UV-Vis spectra of the *Centella Asiatica* leaf aqueuos extract shows absorption at 270 nm and 320 nm which could be assigned to the π-π and n-π transitions respectively in the biomolecules presence in the leaf extract [1] After the addition of *Centella asiatica* leaf extract, it can be clearly seen that the absorption peak assigned to the Pt(IV) ions had almost completely reduced. Therefore, it can be concluded that 10 mL of the *Centella Asiatica* leaf extract was sufficient to reduce Pt(IV) ions into Pt(0). As can be seen from Figure 1 (c), the UV-vis spectrum of the reaction mixture after 30 minutes of reaction somehow showed similarity to that of the *Centella asiatica* leaf extract spectrum. The absorption at 270 nm could be due to the excess biomolecules derived from the plant extract that may surface adsorbed on the formed PtNPs. This finding strongly suggests that the *Centella asiatica* leaf extract has successfully acted as a reducing agent in the formation of Pt(0) from Pt(IV).

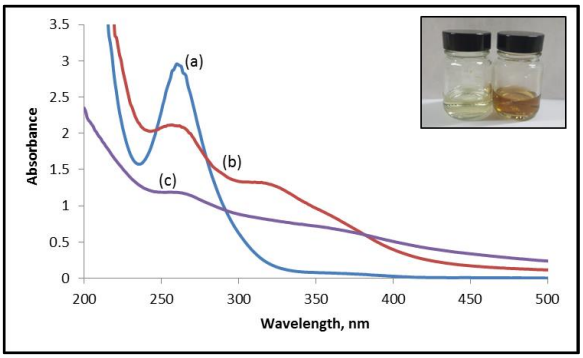

Figure 1. UV-Visible spectra of **(a)** $H_2PtCl_6.6H_2O$ solution **(b)** leaf extract **(c)** PtNPs

3.2. FTIR studies

The FTIR spectrum of the *Centella Asiatica* leaf powder exhibited a broad absorption band centered at 3407 cm^{-1} which can be assigned to the stretching of hydroxyl (-OH) groups, suggesting that the *Centella asiatica* leaf powder contain a significant amount of polyols (phenolic acids and flavonoids) as reported in the literature [5]. The absorption bands observed at 2927 cm^{-1} and around 1626 cm^{-1} could be assigned to the stretching of C─H and C=O, respectively. Meanwhile, the absorption band at 1410 cm^{-1} could be assigned to the O─H bending vibrations. The C─O─H phenolic vibration of polyols appeared at 1263 cm^{-1}. The appearance of these functional groups may be attributed to the presence of antioxidant compounds such as alkaloids, flavonoids, phenols, tannins, terpenoids and saponnins in *Centella Asiatica* leaf powder which has been reported by previous studies.

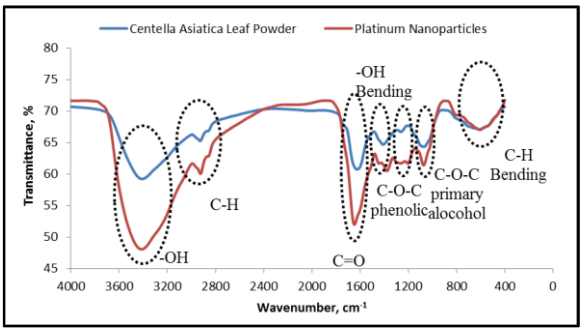

Figure 2. FTIR spectra of *Centella Asiatica* aqueous leaf extract and PtNPs

By comparison, the FTIR spectra of both the PtNPs (Figure 2) shows almost similar FTIR spectrum pattern as the *Centella asiatica* leaf powder. The shift in the O─H stretching and C=O stretching vibrations for PtNPs is possibly due to oxidation of the catechol moiety of flavonoids (quercetin) to their corresponding quinone forms [9]. This observation signifies the involvement of the flavonoids of the *Centella asiatica* leaf extract in the bio reduction process of Pt(IV) ions to Pt(0) and capping the nanoparticles.

3.3. HRTEM

The size and morphology of the biosynthesized PtNPs were investigated using HRTEM analysis. The HRTEM image in Figure 3 illustrates the formation of PtNPs synthesized using *Centella asiatica* leaf aqueous extract. The biosynthesized PtNPs are essentially crystalline and adopt mostly spherical structure. The images show that an amorphous layer can be clearly observed surrounding the PtNPs (Figure 3(b)), probably due to the presence of surface adsorbed biomolecules from the *Centella Asiatica* leaf aqueous extract. As measured by the Gatan software, the clear lattice fringes measured for the PtNPs is 0.233 nm which is in close agreement with previous study [8]. The particle size distribution as shown in the histogram in Figure 3(e) depicted that the particle size of PtNPs ranging from 5 nm to 30 nm with an mean particle size of 10.62 nm ± 1.92 using Image-J software.

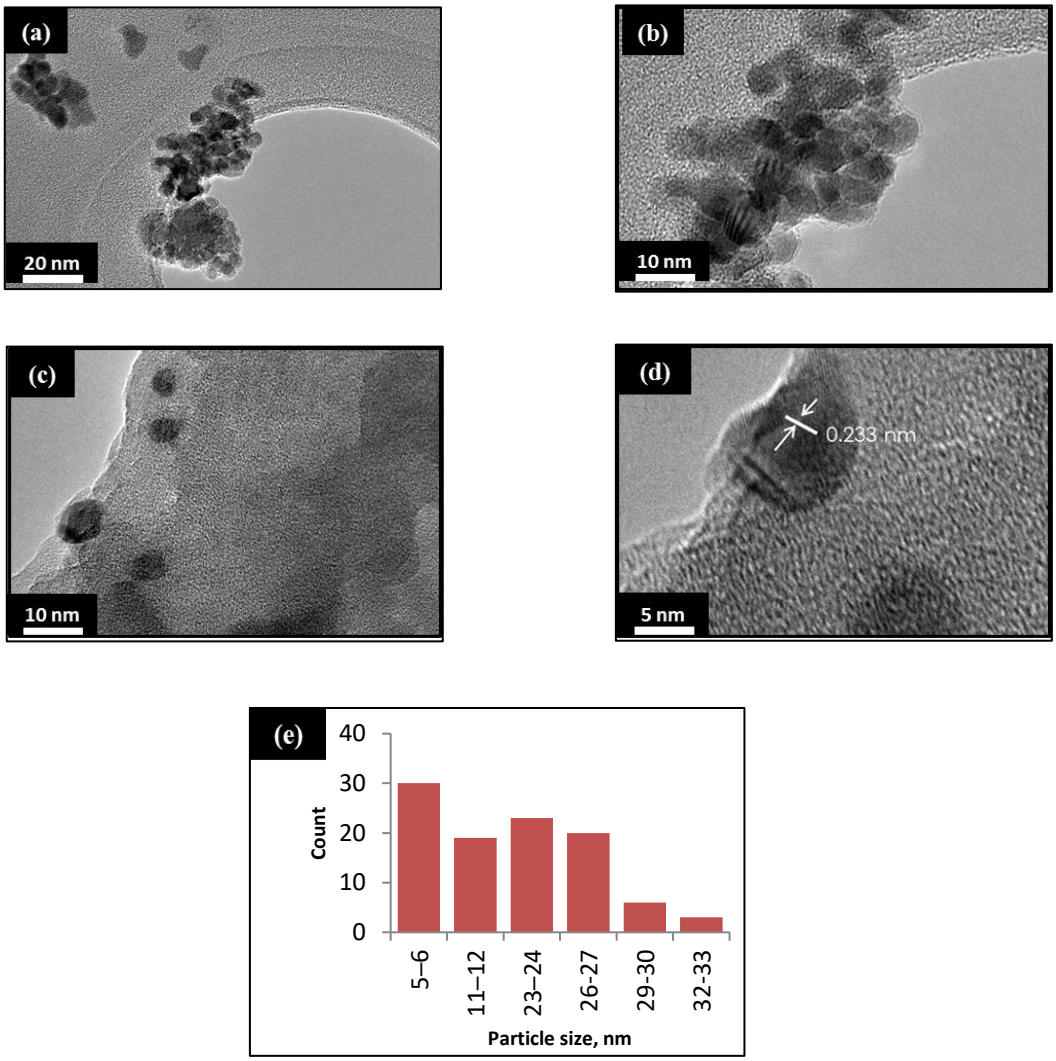

Figure 3. (a), (b), (c), (d) HRTEM image of PtNPs at different magnification (e) particle size distribution measured by image J software

3.4. Catalytic activity in reduction of 4-nitrophenol

In this research, 4-nitrophenol was reduced using biosynthesized PtNPs catalyst in the presence of aqueous $NaBH_4$ as the reductant at room temperature. A model reaction was conducted in reduction of 4-nitrophenol (4NP) to 4-aminophenol (4AP) with $NaBH_4$ to examine the catalytic activity of biosynthesized of PtNPs. It was observed that the reaction mixture turn to yellowish after 4NP was mixed with $NaBH_4$ and showed a maximum absorbance at 400 nm in the UV-visible spectrum due to the formation of 4-nitrophenolate anions in Figure 4 (Sheny et al., 2013). Without the addition of PtNPs as a catalyst, the absorbance of 4-nitrophenolate anion at 400 nm was slightly reduced after 2 hours reaction (Figure 4(a)). The reaction is probably not kinetically favorably process due to large difference in the redox potential of the donor and acceptor couple [7]. However, the absorbance at 400 nm started to decrease following the addition of PtNPs catalyst and concurrent appearance of a gradually intensifying new peak at 300 nm (Figure 4(b)). This new peak at 300 nm corresponded to the reduced product, 4AP [8]. The reduction reaction was completed after 2 hours reaction, in which there were no more changes in 4-nitrophenolate ion absorbance.

A reaction rate was measured from the plot between ln (A_t/A_o) versus time (min) where A_t is the final absorbance and A_o is the initial absorbance. The finding revealed that without catalyst, the linear regression is y = -0.0048x with correlation factor (R^2) 0.09691 indicates that the rate constant of the reduction of 4NP with $NaBH_4$ is 4.8×10^{-3} min^{-1} with 38.9% conversion in Figure 4(c). Herein, with the presence of catalyst, the linear regression equation is y = -0.0186x with

R^2 = 0.9852. From the plot (Figure 4(c)), a pseudo-first reaction is obtained with 1.8×10^{-2} min^{-1} rate constant and 86% of conversion of 4-nitrophenol to 4-aminophenol. The biosynthesized PtNPs providing a suitable reaction surface with lower activation energy and facilitating the transfer of electrons from BH_4^- to 4-nitrophenolate ion. Figure 5 illustrated the reaction of 4-nitrophenol reduced to 4-aminophenol.

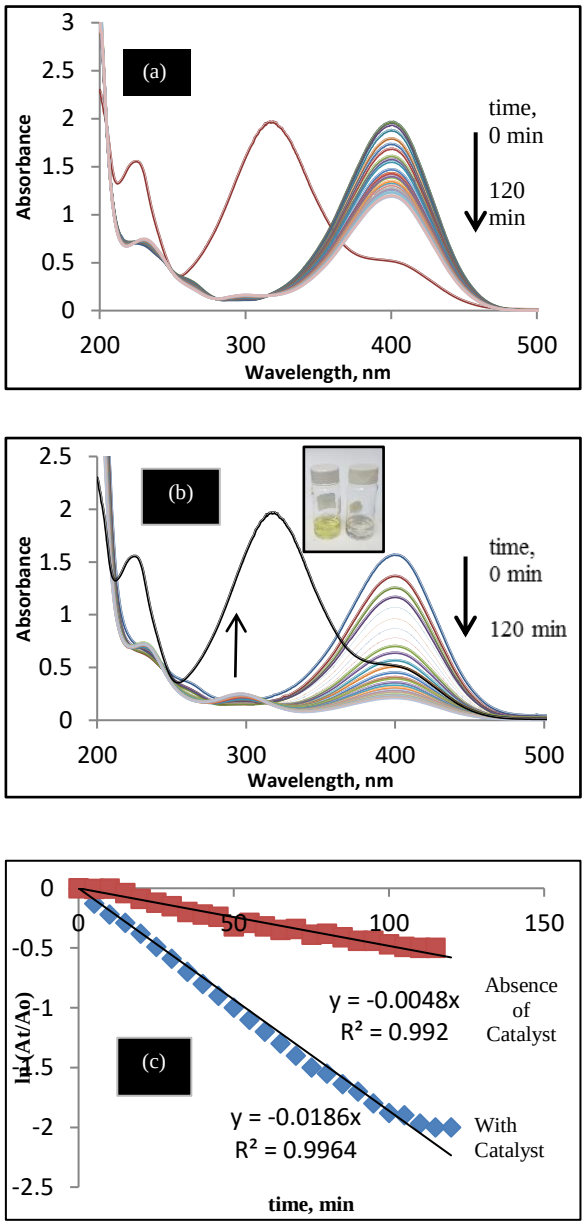

Figure 4. UV-Vis spectra of 4-nitrophenol reduction **(a)** without catalyst, **(b)** with catalyst; **(c)** Plot of ln A_t/A_o versus time (min) for the reduction of 4-nitrophenol

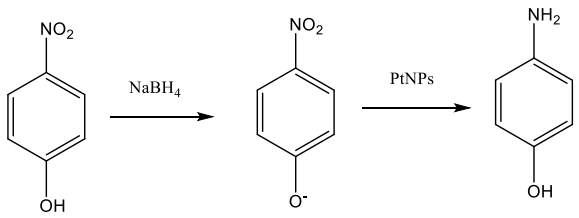

Figure 5. Reduction of 4-nitrophenol to 4-aminophenol with $NaBH_4$ as reducing agent and PtNPs as catalyst

4. CONCLUSION

In this research, we have successfully developed an eco-friendly and green synthesis approach for the synthesizing of platinum nanoparticles (PtNPs) using *Centella Asiatica* aqueous leaf extract. The reduction of Pt(IV) ions to Pt(0) are responsible by the biomolecules of *Centella asiatica* aqueous leaf extract that act as reducing and capping agent on the PtNPs. The formation of PtNPs was proved by UV-Vis Spectroscopy. Similar absorption bands between *Centella Asiatica* leaf powder and PtNPs revealed that the biomolecules act as reductant and capping agent shon by FTIR studies. The morphology of the biosynthesized PtNPs are mostly spherical in shape and HRTEM analysis showed that the lattice fringe is 0.233 nm. The mean of size distribution are found at 10.62 nm ± 1.92. The biosynthesized PtNPs is catalytically active in reduction of 4-nitrophenol achieving 86.6% conversion, follows a pseudo-first order reaction with rate constant value at 1.86×10^{-2} min^{-1}.

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