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Green synthesis of Pd NPs from Pimpinella tirupatiensis plant extract and their application in photocatalytic activity dye degradation

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Abstract. The present report the synthesis of palladium nanoparticles through the green method route offers few advantages over the common chemical and physical procedures, as it is an easy and fast, eco-friendly and does not involve any costly chemicals as well as hazardous chemicals. In this study, we reported synthesis of Pd NPs by using the Pimpinella tirupatiensis plant Extract (PTPE). The synthesized Pd NPs was characterization using different technique such as UV-Visible for the formation of Pd NPs. FT-IR spectroscopy was performed to detect the bio-active molecules liable for reduction and capping of biogenic Pd NPs. Crystallinity of Pd NPs conformed by powder – XRD. In the present study performed photo catalytic activity of synthesized Pd NPs using organic dye such as Congo red (CR). Hence, this study concludes the PTPE aqueous extract produced Pd NPs can be act as promising material for the degradation of organic pollutants.

1. Introduction

Nanotechnology deals with tuning of particles size with different morphology and nanostructures. Hence nanotechnology has been applied to many challenging fields with improved properties of nanomaterials. Nowadays metallic nanoparticles are used in catalysis, photonics, nanoelectronics and sensing [1-3]. Among various metallic nanoparticles, palladium nanoparticles Pd NPs have several unique applications, and there are various classical and fundamental methods described in the literature for the synthesis of Pd NPs. They can be synthesized by chemical [4-6], electrochemical or sonochemical methods. Anyway, presently there are several chemical and biological [7,8] methods available for making of some of the metallic nanoparticles such as silver, gold and Palladium nanoparticles, but in spite of great usage of Pd NPs in industry and bio systems, such as the best catalytic roles in fuel cells, organic reactions [9] and etc., there are limited biomimetic approaches has been reported for preparation of these nanoparticles [10].

Out of different methods for synthesis of nanomaterials green synthesis approach has received much attention being environmentally benign technology [11]. Hence Palladium nanoparticles were synthesised using the plant extract which shows the photo-catalytic activity and uses as a catalyst for organic dyes. With the help of organic dyes the catalytic activity of Pd NPs were observed. Hence Pd NPs have good catalytic activity against organic dyes [12, 13].

During last decades disposal of dye based pollutants is a severe concern among many issues that challenge our environment. Dyes are a major class of synthetic organic compounds released by many industries such as plastic, paper, food, and tanneries, pharmaceutical, cosmetic and textile industries. The colour content in dye adsorbs and reflects sunlight inflowing the polluted water, thereby hindering photosynthesis and interfere the development of aqua species. Degradation of these compounds to non-toxic products is difficult because of their high stability. Metal nanoparticles (M NPs) have received great attention due to their catalytic role in the degradation of organic dyes. Various reports are available on the NPs mediated catalytic degradation of organic dyes using photo reactor [14]. Being primary catalyst palladium nanoparticles (PDNPs) finds its application in low temperature reduction of automobile pollutant, organic reactions and hydrogenation [15, 16].

Palladium nanoparticles were characterized using different analytical methods as UV-Visible spectroscopy for identifying the formation of nanoparticles, FTIR spectroscopy for identifying the functional group, X-ray diffraction pattern (XRD) for identification of structure of nanoparticles. Finally catalytic activity of Congo red as degradation of colour also studied [17, 18].

2. Material and methods

2.1 Materials

Palladium chloride ($Pdcl_2$)**,** sodium borohydride ($NaBH_4$), organic dyes such as Congo red (CR), was purchased from Sigma-Aldrich, Mumbai. Other reagents are of analytical grade and Milli-Q water was used throughout the study.

2.2 Experimental procedure

The reagents used are under analytical grade reagents which pure. Palladium chloride was weighed and dissolved in deionised water throughout the experiment. The leaves of the plant was collected and dried and finely powdered and 3 g of the Pimpinella Tirupatiensis leaf powder was weighed and dissolved in 100 ml water in Erlenmeyer flask. The solution was kept for heating at 60ºc in a hotplate for 30 minutes and cooled to room temperature. Filtration of the solution was carried out with whatmann no.1 filter paper. After filtration the extract was kept in 4ºc for the preparation of nanoparticles. Palladium nanoparticles were prepared by adding 30 ml of the plant extract to 15 ml of 5 mM Palladium chloride and place it in magnetic stirrer for 2 hours at 60 ºC. The brown colloidal solution of palladium nanoparticles was obtained. Colloidal solution was centrifuged at 2000 rpm for 30 minutes, the Palladium nanoparticles would settle down as residue and the residue were collected and the supernatant liquid was discarded. The residue was extracted twice with ethanol and once with double distilled water. The spectroscopic studies were carried out to confirm the formation of Palladium nanoparticles such as UV-Visible for identifying the formation of nanoparticles (Figure 1). FTIR was used for identifying functional groups present in nanoparticles, XRD analysis was carried out for identifying the structure of nanoparticles.

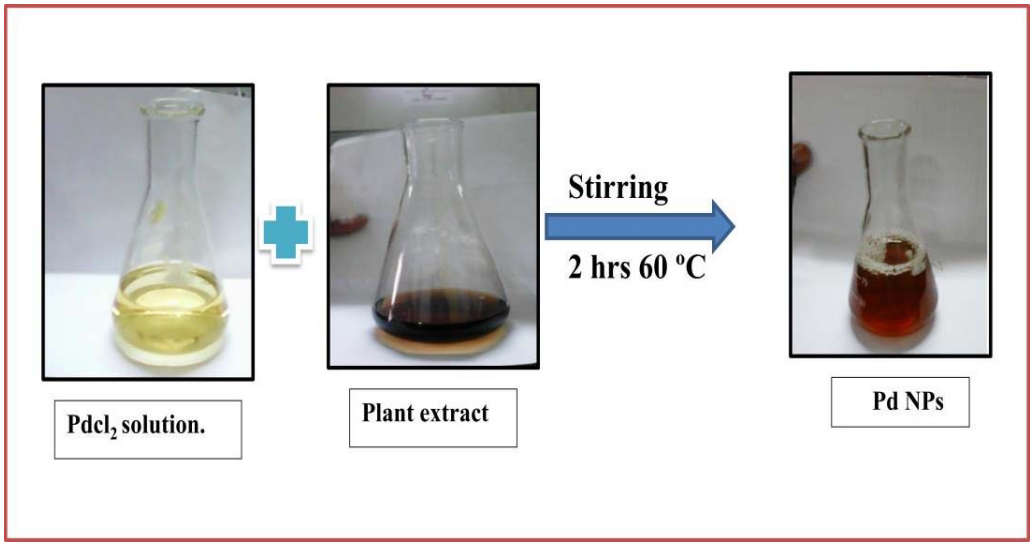


Fig 1. Experimental procedure for the synthesis of Pd NPs

2.3 Characterization of synthesized Pd NPs

2.3.1 UV-Visible spectroscopy analysis (UV-Vis)

The initial characterization of the synthesized Pd NPs was carried out by a UV-visible spectroscopy (Jasco V-670 UV-visible spectrophotometer). The spectra were recorded in between wavelength range 200 nm to 800 nm, and the generated data was plotted using Origin 8.0 software.

2. 3. 2 *Fourier Transform Infra Red analyses (FTIR)*

The capped functional groups on the nanoparticles surface was detected by recording FTIR spectra of purified dried Pd NPs (Shimadzu IR AFFINITY-1, JASCO FT-IR 4100) against ECBP's powder as control in diffuse reflectance mode at a resolution of 4 cm. Pure untreated dry ECBPs powder was checked under the same instrumental conditions as quality standard.

2. 3. 3 X-ray diffraction analysis (XRD)

Dried powder was used for XRD and FT-IR analysis. The XRD analysis of dried Pd NPs was carried out by a Bruker D8 Advance diffractometer with Cu Kα radiation ($\lambda=1.54^0$). The diffractogram was recorded against 2θ value of 10^0 to 90^0 with a scanning rate of 4^0 per min and a step size of 0.02^0.

2.3.4 Transmission Electron Microscope (TEM) analysis

JEOL-JEM 2100 Transmission Electron Microscope with an acceleration voltage of 200kV was used to resolve the morphology of Pd NPs. 200 µL of the Pd NPs colloidal solution was dispersed in 1mL deionised water in an ultrasonic bath and analysed by placing drops of solution over the carbon-coated grids and dried at ambient temperature.

3. Results and Discussions

The formation of Pd NPs was initially observed visible colour change and then confirmed by UV-Visible spectroscopy. The reduction of Pd^{+2} to Pd^{0} nanoparticles was instantaneous i.e. when extract add to palladium solution resulted reduction and visual colour change light yellow to dark brown colour solution, this indicates the formation of Pd NPs which was confirmed by UV-Visible spectroscopy study. The characteristic SPR band at 260 nm indicated the formation of Pd NPs Figure 2.

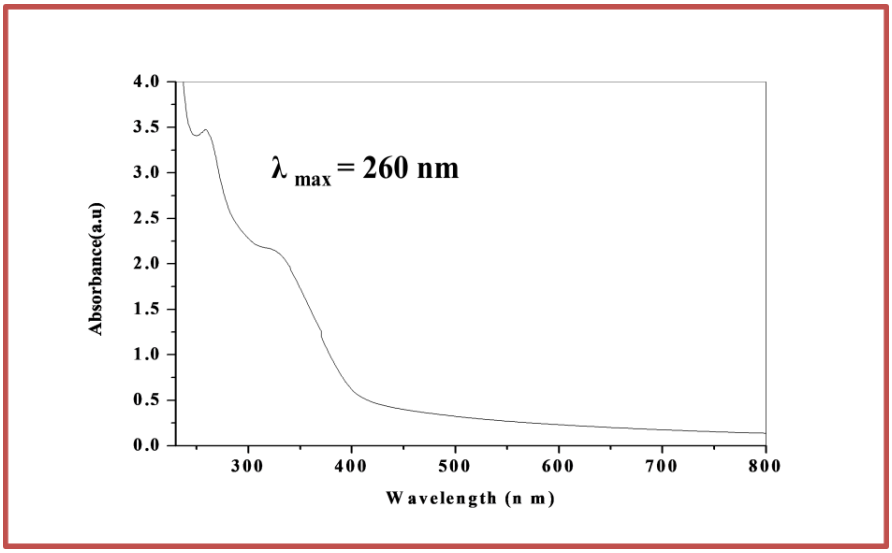


Figure 2. UV-Visible spectra for the formation of Pd NPs

XRD pattern of synthesized Pd NPs showed characteristic diffraction peaks at 39.55^{0}, 46.22^{0}, 67.57^{0} which corresponds to the (111), (200), (220) plants of face centred cubic crystal (FCC) structure Figure 3. The lattice constant and diffraction peaks values were confirmed by JCPDS card No 96-101-1111. The sharp peak indicates the high crystalline nature of Pd NPs. The average crystalline size was calculated by using Debye-Scherer formula.

The average crystalline size was calculated in Debye-Scherred equation

$$D = K\lambda/\beta Cos\,(\theta)$$

Where D is the average crystal size, λ is the X-ray wavelength (λ =1.5406 A^{0}), K is the Scherrer coefficient (0.891), β, full width at half maximum intensity (FWHM) in radians, θ is Bragg's angle (2θ). The average crystalline size was 15.4 nm.

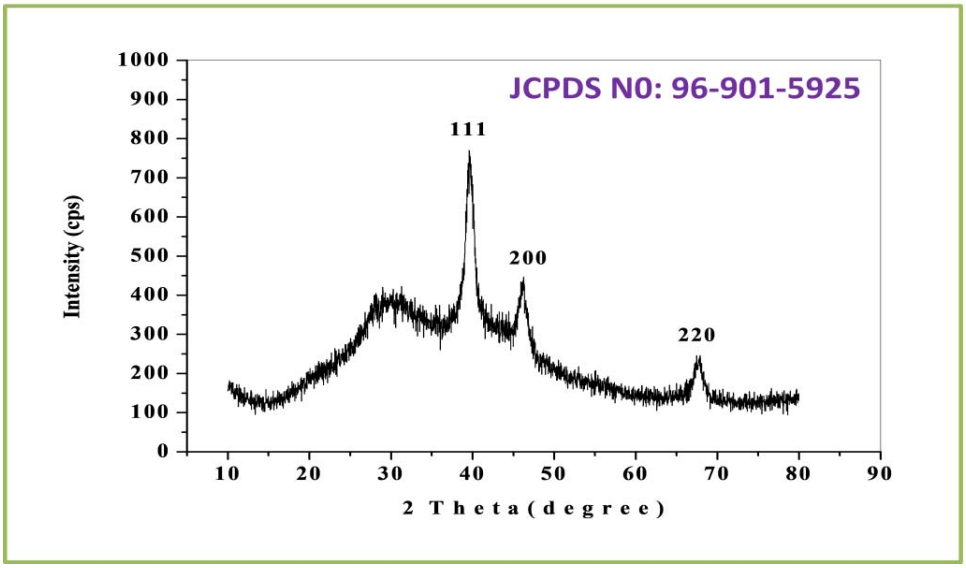


Figure 3. X-ray diffraction pattern of synthesized Pd NPs.

Multifunctional groups of plant extract was analysed by FT-IR spectroscopy studies after recording spectra of plant extract before and after reduction along with purified Pd NPs. FT-IR spectra of Pd NPs demonstrated bands at 3311.78 cm^{-1}, 78.34 cm^{-1}, 1724.36 cm^{-1}, 1627.24 cm^{-1}, 1369.46 cm^{-1}, 1139.93 cm^{-1}, 1195.87 cm^{-1}, 1089.78 cm^{-1}; which plant extract demonstrates bands at 3215.13 cm^{-1}, 2960.11 cm^{-1} 1726.29 cm^{-1}, 1587.42 cm^{-1}, 1373.32 cm^{-1}, 1213.23 cm^{-1}, 1068.59 cm^{-1}, the bands at wave number of 3311.75 cm^{-1}, 2960 cm-1, 1724.36 cm^{-1}, 1627 cm^{-1}corspondng to ⁻OH stretching of phenolic compounds, aromatic ⁻C⁻H stretching, carboxyl ⁻C= O stretching, ⁻C⁻O and ⁻C⁻O⁻C⁻ stretching respectively Figure 4. The FT-IR spectroscopy results show the presence of multifunctional groups on the palladium metal of the surface. This indicates that stability of Pd NPs is due to bio molecules capping onto the surface through electrostatic interaction indicating the potential of plant good stabilizing agent.

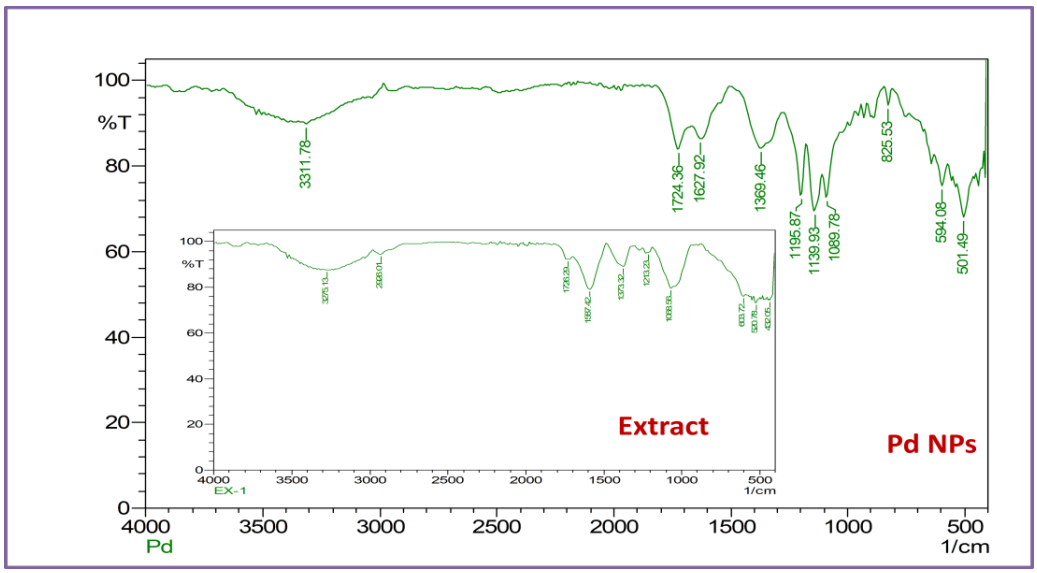


Figure 4. FTIR spectra of synthesized Pd NPs and inset Pimpinella tirupatiensis plant extract.

Morphology, size and shape of synthesised Pd NPs were investigated by TEM analysis. Figure 5(A-C). Presents visualised images of the synthesis Pd NPs. The images expose the formation of spherical Pd NPs which is in clear agreement with UV-Visible data. The average size of the Pd NPs was 12.25 nm. Biomolecular capping onto the surface of the Pd NPs were evidenced by TEM analysis which shows the thin layer of organic coating of the Pd NPs surface and it was further confirmed by FTIR study. The crystalline nature of Pd NPs was further confirmed by SAED pattern Figure 5(D)**.** Which shows the diffraction rings with bright spots and are indexed to (111), (200), and (220) crystal planes of the face centered cubic structure.

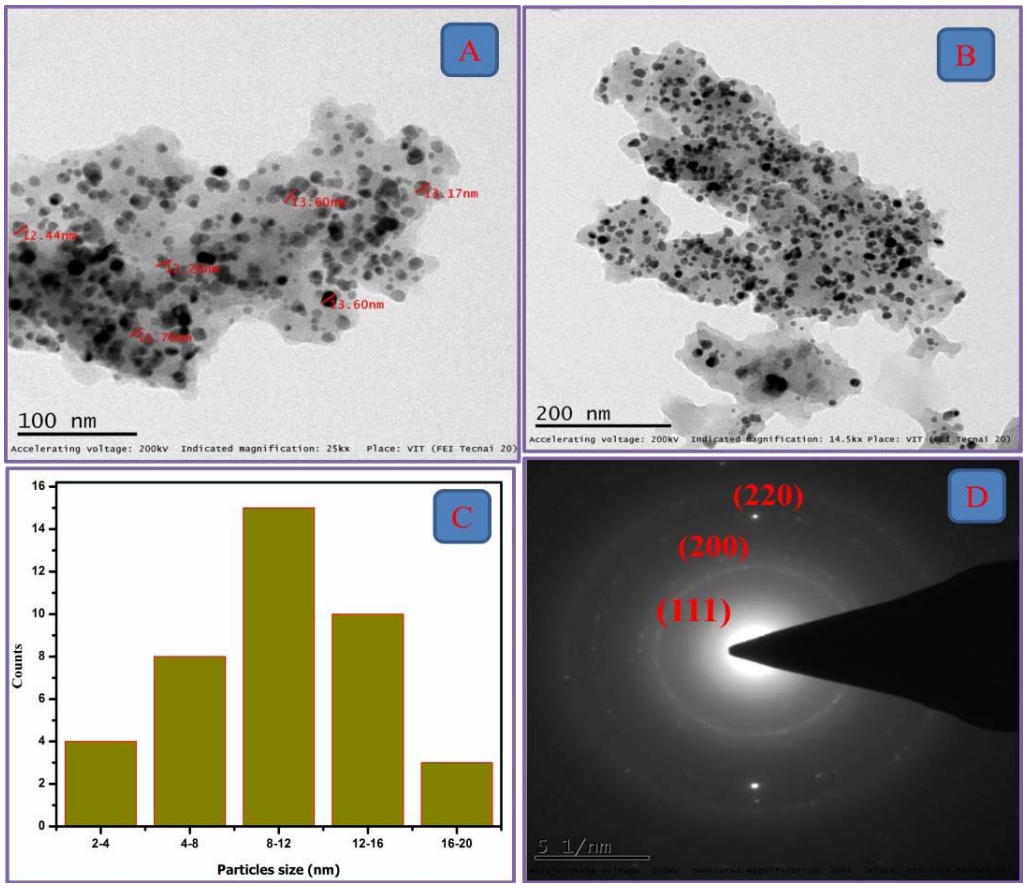


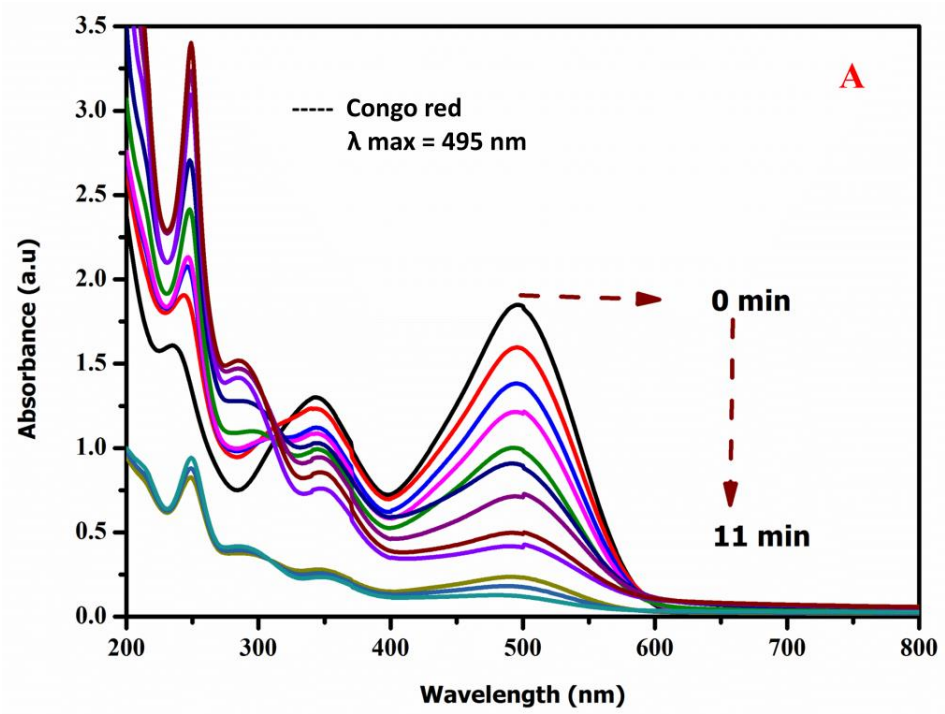
Fig 5. (A, B) Visualised images of HR-TEM and (C, D) represent the Average particles size distribution and SAED pattern.

3.1 Catalytic activity of Pd NPs

The organic dye Congo red is a typical representative of high toxic and common organic pollutants in industrial and agriculture wastewater. Effluents of textile dyeing industry causes serious effect due to chemical changes of dyes under environmental conditions and the transformed products may be more toxic. Hence organic dyes were considered as reprentative pollutant for this catalytic degradation study. These are readily soluble in water. Initially, the addition of $NaBH_4$ did not degrade the dyes, but by the addition Pd NPs the dyes degraded within few minutes [19, 20].

3.2 Catalytic activity of Pd NPs for degradation of Congo red (CR)

The degradation was attempted in the absence of Pd nanoparticles in process did not show any progress till test duration 60 min in Figure 6(B). The sodium borohydride unable to carry out reduce the dye degradation. The reduction of dye by sodium borohydride without catalyst may be favourable thermodynamic standard point but not kinetically due the reduction potential between electron donating sodium borohydride and electron accepting Congo red dye is huge. Electron transfer between two species is very difficult this makes reduction process more cumbersome. The Biosynthesized Pd nanoparticles added to the solution contains Congo red dye and sodium borohydride. The high surface area offered by the nanoparticles provides the increase the reduction reaction rate. Under the standard point of chemical environment sodium borohydride can effectively reduced the Congo red dye its leading to degradation occurs rapidly. When nanoparticles added to dye solution, its helps the in shuttling electron" In the process by passing of electron to acceptor from the donor. The degradation of Congo red dye is mainly depended on nanocatalyst mediated transfer of electrons.



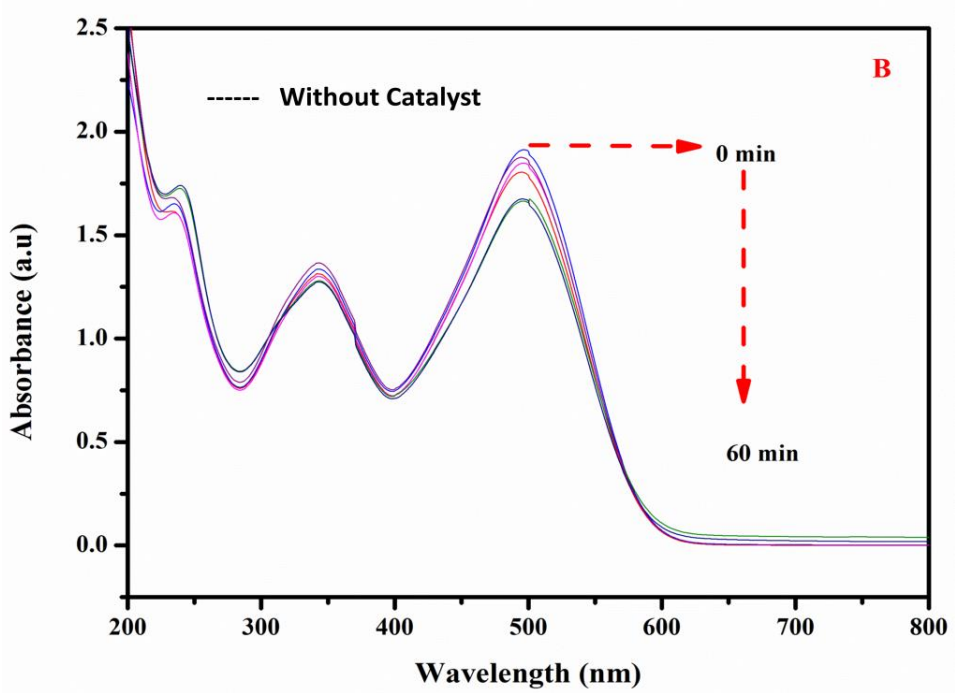


Figure 6. UV-Visible spectra for the degradation of Congo red dye by $NaBH_4$ in the presence of Pd NPs (A) and without Pd NPs (B).

Figure 6(A). Shows the time dependent UV-Visible spectra of Congo red (CR) catalysed by Pd NPs. During the degradation process, in one test tube, 3 ml Congo red (10^{-4} M) was taken and 500 µl $NaBH_4$ (0.05 M) was added and finally 300 µl Pd NPs (mg/mL) were added to the concentration of Congo red dye solution, the colour was rapidly decreased and finally disappeared with in 11 min at 495.67 nm. It represented the formation of Leuco Congo red (LCR). The catalytic degradation of CR yielded LCR without by-product [21, 22]. As concentration of $NaBH_4$ was very high, the degradation rate was independent on $NaBH_4$ concentration and pseudo-first order kinetic equation was considered to calculate the catalytic rate Figure 7(A). The absorbance of CR was proportional to its concentration and rate constant k was 0.12805 min^{-1}[23].

The degradation efficiency of Congo red dye was calculated by using formula that is

$$(\%) \text{ of the degradation} = \left[\frac{C_0 - Ct}{C0} \right] 100$$

Here.... C_0 is initial concentration of dye absorbance

Ct is the time taken for interval dye degradation of absorbance

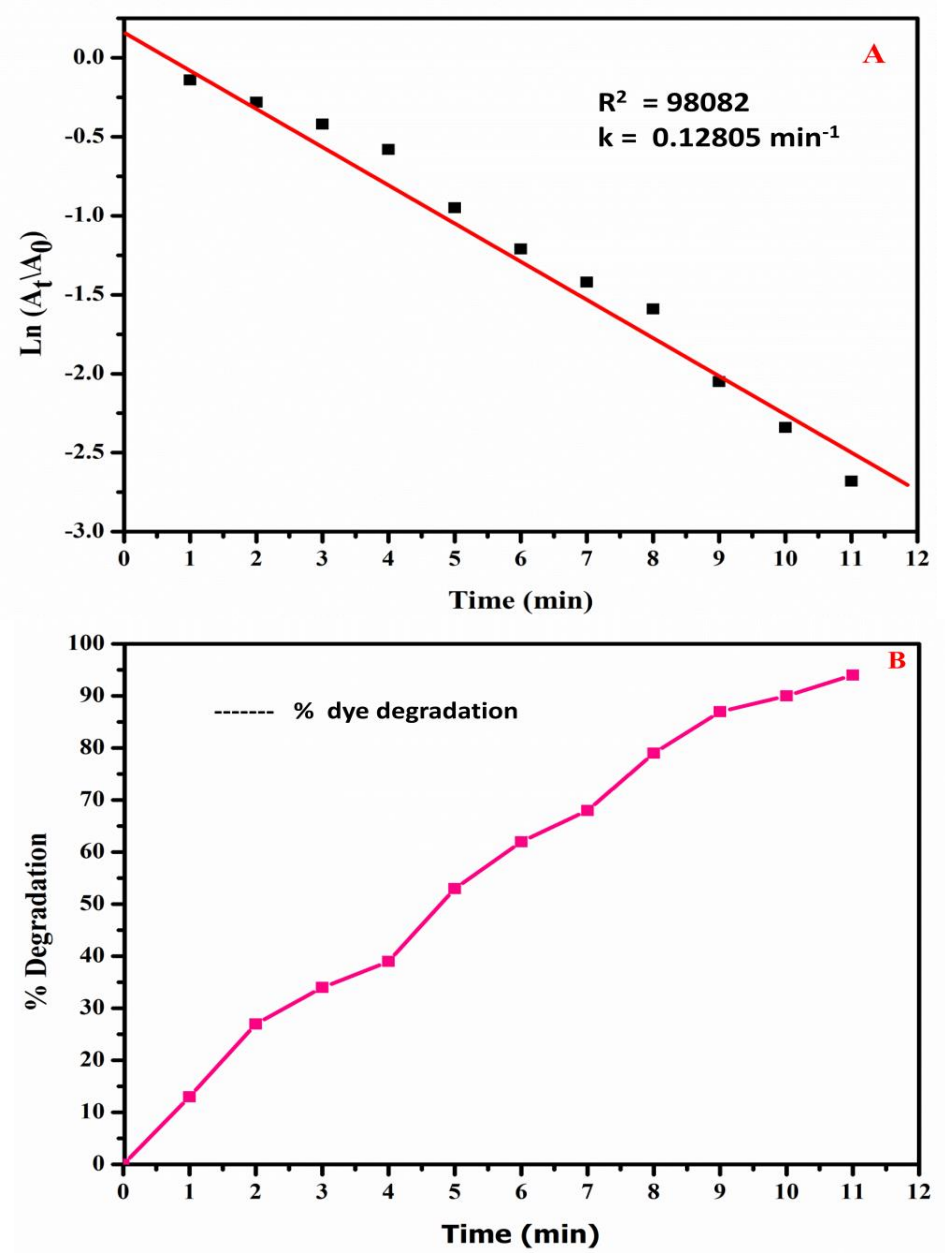


Fig. 7 The kinetic of catalytic activity (A) and % of the Congo red dye degradation (B).

In Figure 7(B). Show the percent of the dye degradation. The obtained result shows the 94% degradation. The degradation is depends on the different factor such as size of the nanoparticles and surface area. The concentration dyes and the amount of the sodium borohydride such as sufficient of hydride ions it's leading to electron transfer to accepting of target molecules (dye). In Figure 8. Show the Congo red dye degradation of possible mechanism. The hydride ion transfers to target molecules such as azo bond diminish via...single electron transfer of between nitrogen bond and then formation of new bond between nitrogen and hydrogen. In figure clearly show the colour changes is visualised.

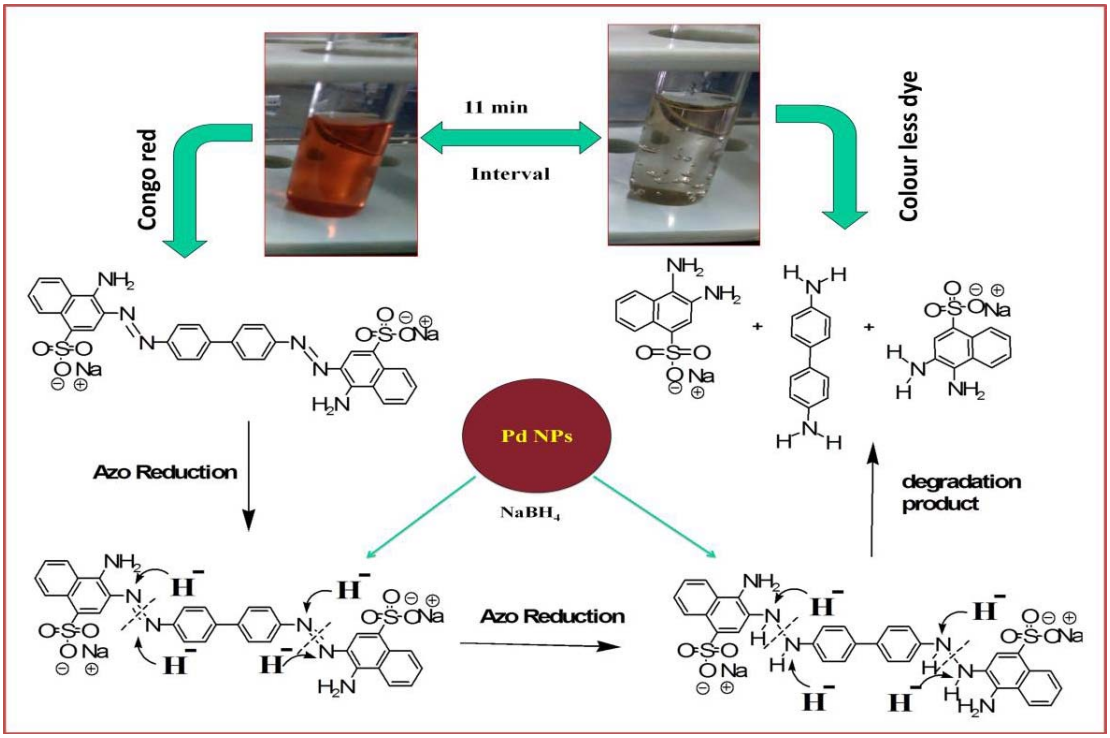


Fig. 8 The possible mechanism of Congo red dye degradation in the presence of $NaBH_4$.

3. Conclusion

In this respect a simple and efficient way to synthesize and stable Pd NPs using Pimpinella Tirupatiensis plant extract. The synthesized Pd NPs were initially confirmed by using UV-Visible spectroscopy and crystalline nature of Pd NPs were evidenced through XRD studies and multifunctional groups of plant extract were confirmed by FTIR. The synthesised Pd NPs showed good catalytic activity in the degradation of organic dyes such as Congo red using $NaBH_4$ as reducing agent. In this study, degradation of organic dye Cong red was done using Pd NPs as a catalyst. The significant catalytic performances of Pd NPs are due to their high surface to volume ratio providing more active sites of the reactant molecules to interact. The colloidal solution was stable, suggesting that extract can be used as both reducing and stabilizing agent for the preparation of Palladium nanoparticles.

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