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Green synthesis, characterisation and biological activity of Platinum Nanoparticle using Croton Caudatus Geisel leaf extract

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Abstract: - In this present study we explore the reducing and capping potential of aqueous leaf extract from Croton Caudatus Geisel for the synthesis of platinum nano particles. The colour change and UV visible spectroscopic analysis reveals the surface plasmon resonance (SPR) of the final reaction product which confirms the reduction of platinum (IV) into platinum nano particles. FT-IR, XRD, SEM-EDX, TEM studies confirms the strong reducing potentials of Croton Caudatus Geisel leaf extract which can also be tested in the green synthesis of other metallic nano particles.

Keywords

Nanoparticle, Croton Caudatus Geisel, UV Visible spectro photometer, FTIR, XRD, SEM-EDX, TEM.

1. INTRODUCTION

Nano chemistry is gaining tremendous impetus in the present century due to its capability of converting metals into their nano particle size. Research in nano chemistry highlights the possibility of green chemistry pathways to produce industriously important nanoparticles[1, 2]. Nano particles can be synthesized using various approaches including chemical, physical and biological. Although chemical method of synthesis requires short period of time for the synthesis of large quantity of nano particles, this method requires capping agents for size stabilization of the nanoparticles. Chemicals used for nano particles synthesis and stabilization are toxic and lead to non ecofriendly byproducts. The need for environmental non-toxic synthetic methods for nanoparticles synthesis leads to the developing interest in biological approaches which are free from the use of toxic chemicals as byproducts. Thus, there is an increasing demand for ‘‘green nanotechnology’’ [3].Platinum as catalysts enables power generation in fuel cell vehicles, electro catalysis and chemical synthesis (also in silver–platinum nanoparticles) as a magnetic nanopowder and deposed on silica and carbon nanotubes. Microbial synthesis of nanoparticles such as sulphate reducing bacteria was used to investigate the enzymatic mechanism for the total bioreduction of platinum (IV) into platinum (0) nanoparticles by cytoplasmic hydrogenase and periplasmic hydrogenase [4]. Platinum nano particles are usually used in the form of colloid or suspension in a fluid. Synthesis of platinum nanoparticles was achieved by Song et al.[5] using the leaf extract of Diopyros kaki. They reported that more than 90% of the platinum ions were converted into nanoparticles using 10% leaf biomass concentration at 95°C, and the average size of synthesized nanoparticles ranged from 2 to 12 nm. Coccia et al [6] reported one-pot synthesis of platinum and palladium nanoparticles using lignin isolated from red pine (Pinus resinosa). Rapid synthesis of platinum nanoparticles has also been reported by Soundarrajan etal. [7] Croton Caudatus Geisel is widely distributed in South East Asia(Shantabi etal., 2014)[8]. It usually grows in evergreen forests and also grows near marginal areas along river or stream tracts. In Mizoram, they are usually available at an altitude between 500m to 9000m. The Croton caudatus Geisel has been traditionally used to treat several human health disorders. It is used as a poultice to treat fever and sprains in various parts of Asia. It is also used to treat liver diseases. The roots of Croton caudatus are purgative and its roots, stems or leaves are used individually or even the whole plant is also used for medicinal purpose owing to low toxicity[9].It is being used as a traditional medicine for the treatment of diseases particularly cancer and related diseases. The plant is locally called Sai ekhlo (Mizo). Because of these strong medicinal properities, we investigate a novel synthesis of platinum nanoparticles biosynthesized with Croton Caudatus Geisel Leaf extract and their preliminary biological activity. In recent years plant mediated biological synthesis of Nanoparticles is gaining important due to its simplicity and eco friendly approaches. One more fundamental level is that, it would be interesting to study the nature of nano particles formed using extracts of different parts of plants. A survey of literature reveals that the plant extract of Croton Caudatus Geisel has not yet been used for synthesis of platinum nanoparticles.

II..METHODS AND MATERIAL

2.1 Sample Collection:
The fresh leaves of Croton Caudatus Geisel were collected from Karaiyar village in Tirunelveli district of Tamil Nadu, India.

2.2Preparation of Croton Caudatus Geisel leaf extract:
The fresh leaves were individually collected and washed thoroughly with cold water and then with distilled water, up to 10 days shade dried and fine powder was prepared by using mechanical grinder. 2gram of the fine powder was mixed with 200 ml deionized water and the mixture was kept at 95oC for 45 minutes with vigorous magnetic stirring. This was filtered with Whatmann no.1 filter paper to get clear aqueous extract. This extract was stored in a refrigerator for further studies.

2.3Synthesis of platinum nanoparticles:
Hexachloroplatinic acid ($H_2PtCl_4.H_2O$) was purchased from Merck specialties limited Mumbai was used in the synthesis of platinium nanoparticles using Croton Caudatus Geisel leaf extract. Hexa chloro platinic acid was prepared at the 1×10^{-3} M concentration with double distilled water. 10 ml of the leaf extract was mixed with 90 ml of 1mM Hexa chloroplatinic acid for the synthesis of platinum nano particles. The solution was mixed under magnetic stirring for 1 hour at the temperature of 48oC.The color of the mixture is yellow to dark brown .This colour change is clearly indicate that the reduction of platinum (Pt^{4+}) to Pt .

III. CHARACTERISATION OF SYNTHESIZED NANO PARTICLES

3.1 UV-Visible spectro photo meter:
The platinum nano particles were confirmed by colour changes that is dark brown and confirmed by UV Visible spectro photo meter on Ocean Optics-UV-Vis Spectrophotometer, Model number:USB2000 .

3.2 Fourier Transform Infra Red Spectroscopy:
The Fourier Transform Infra Red Spectroscopy used for the analysis of reduced gold. The spectrum was taken in the mid- IR range of 500 to 4000 cm^{-1}. With 25 scan speed. The sample were mixed with pure KBr crystals in the ratio of 1:100 and the crystals were fixed in the sample holder for the entire analysis. The instrument used for this analysis is SHIMA DZU IR TRACER -100.

3.3 XRAY diffraction:
The platinum nano particles of Croton Caudatus Geisel was purified and get pure crystals. The composition of nano particles were analyzed by XRD. The dried mixture of nano particles were used for the determination of the formation of gold nano particles by BRUKER ECO D8 ADVANCE X- ray diffractiometer operated at a voltage of 40kV and a current of 20mA with copper $K\alpha$ radiation in θ-2θ configuration. The crystallite domain size was calculated from the width of the XRD peaks assuming that they are free from non-uniform strains using the Debye Scherrer's formula

$$D = 0.94 \lambda / \beta \cos \theta$$

Where D is the average crystallite domain perpendicular to the reflection plane:

λ is the x ray wave length
β is the full width at half maximum
θ is the diffraction angle.

3.4 Scanning electron microscopy(SEM) and EDAX analysis:
Scanning electron microscopy (SEM) analysis was done by using VEGA3TESCAN machine. Thin films of the sample were prepared on a carbon coated grid by just dropping a very small amount of the sample on the grid, extra solution was removed bussing blotting paper and the film on the SEM grid were allowed to dry by putting it over a mercury lamb for few minutes.

3.5 Transmission Electron Microscopy (TEM):
Transmission electron microscopy (TEM) is microscopic technique were by a beam of electron is transmitted ultra thin specimen, interacting with the specimen as it passes through. platinum nano particle image was formed from the interactions of electrons transmitted through specimen.

IV. RESULTS AND DISCUSSION

4.1 UV visible spectrophotometer:
Qualitative analysis of the colour change of the platinum (IV) solution from light yellow to dark brown[10,11,12] indicates of the formation of platinum (0)Which is shown in figure 1.Also the reduction of aqueous $H_2PtCl_4.H_2O$ ions during the reaction with plant extract of Croton Caudatus Geisel was followed by UV-Visible spectroscopy. The following fig 2 represents the UV-Visible absorption spectrum recorded from the Croton Caudatus Geisel extract prepared from aqueous platinum nano particle solution. A strong absorption peak at 302 nm which confirms the presence of platinum nano particles.

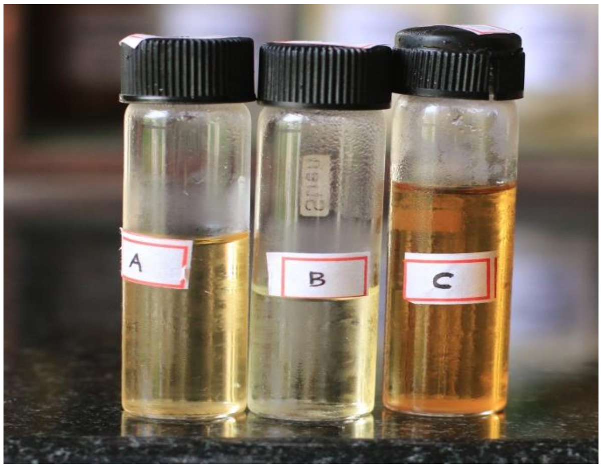

Figure1. Visual observation of platinum nano particle synthesis
(A-Plant extract   B-salt solution   C- reaction mixture)

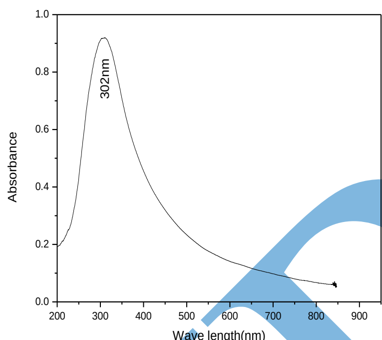

Figure2. UV –visible spectrum of synthesized Pt NPs showed peak at 302nm

4.2 FT-IR analysis:

FT IR analysis can provide information about functional groups present in the synthesized gold nano particles for understanding their transformation from simple inorganic $H_2PtCl_4.H_2O$ to elemental platinum by action of the different phytochemicals present in the Croton Caudatus Geisel leaf extract. These phytochemicals acts as capping agent for the nano particles. FTIR spectra of the palmyra sprout root extract and the synthesized gold nanoparticles, as shown in Figure3 can offer information regarding the chemical change of the functional groups involved in the reduction. The FTIR spectrum of the Croton Caudatus Geisel leaf extract showed band at 3,581, 1,676, 1,411 and 1,064 cm-1. The strong broad absorbance at 3,581 cm-1 is the characteristic of the hydroxyl functional group in alcohols and phenolic compounds. The band at 1,676 cm-1 can be assigned to the functional group in alkenes.The band at 1,411 cm-1 corresponds to the C– C stretch(in-ring) aromatic compounds. The band at 1,064 corresponds to the –C-N stretch of aliphatic amines. Hence biomolecuels, aminoacids present in the leaf extract which acts as reducing agents for platinum ions reduction.[13,14,15]. Also the figure illustrates the successful bio fabrication platinum nano particles mediated Croton Caudatus Geisel leaf extracts.

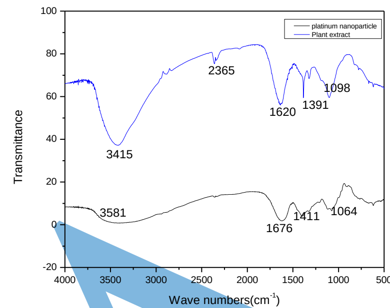

Figure3: FT IR spectrum of synthesized platinum nano particle of Croton Caudatus Geisel and plant extract

4.3 XRD analysis:

The exact nature and size of the synthesized nano particles was studied through XRD analysis. Figure4 shows the strong and narrow diffraction peaks indicated that the product have well crystalline. The XRD peaks at 38.4o,44.6 oand 64.0 o can be index to the (111),(200)and (220).The Bragg's reflection of cubic structure of metallic platinum respectively. A strong diffraction peak located at 38.4o was ascribed to the (111) facets of face centered cubic metal platinum structure, while diffraction peaks of other facets were much weaker. The broadening of Bragg's peaks provided additional indication for the information of platinum nano particles. The width of the (111) Bragg's reflection was determined for calculating the mean size of Au nano particles by using Debye Scherrer's equation which was found to be around 10.3nm

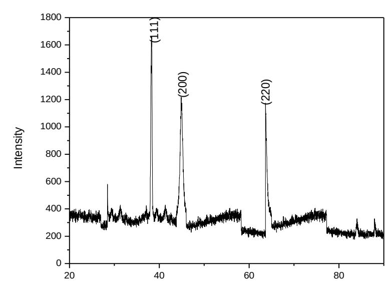

Figure4: X-ray diffraction patterns of synthesized Pt NPs.

4.4 SEM-EDX analysis:

To determine the shape, size and distribution of the nanoparticles, SEM Images were recorded. The SEM analysis confirmed the synthesized gold nanoparticles to be in nanometer size. They were spherical in shape and the size of the gold nanoparticles found to be uniformly distributed Figure5. The size of the gold nanoparticles varies in SEM compared to that of XRD analysis. This may be due to the capping nature of the phytoconstituents as the time increases from the day of synthesis.

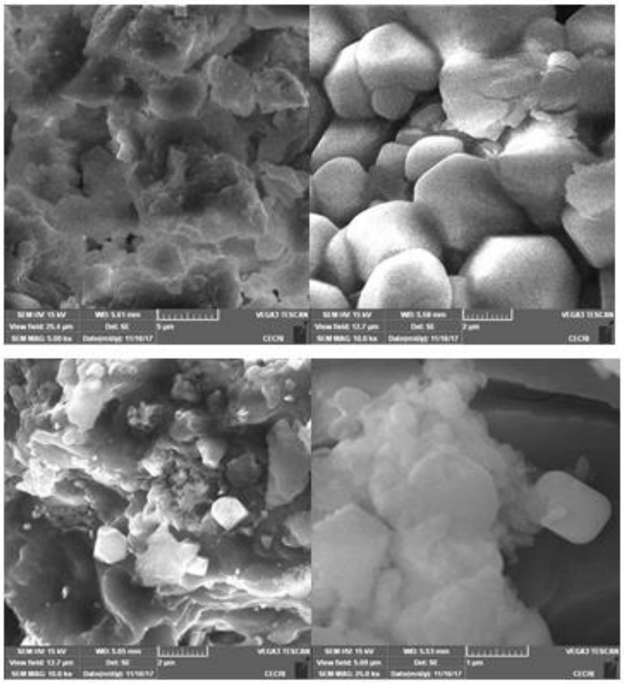

Figure 5: SEM images of platinum nano particles at different magnifications

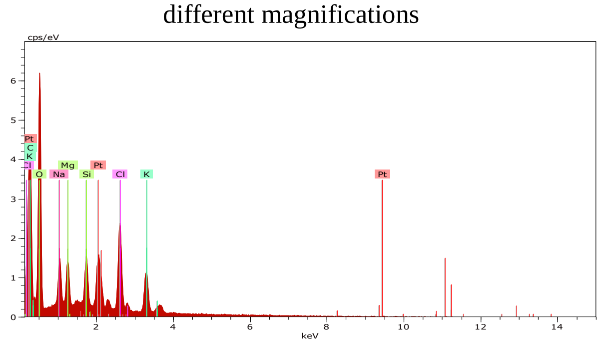

Figure6. EDX spectrum of platinum NPs capped with Croton Caudatus Geisel leaf extract

Elemental composition:

Element	Weight%	Atom %
Oxygen	46.66	50.77
Carbon	25.57	37.06
Platinum	8.03	0.72
Chlorine	6.39	3.14
Potassium	4.25	1.89
Sodium	3.77	2.86
Magnesium	2.73	1.95
Silicon	2.60	1.61

4.5 TEM analysis:

The size and shape of the synthesized AuNPs were confirmed by TEM analysis. Figure7 shows that AuNPs synthesized, were mainly spherical along with a few irregular shapes. It is obvious that the resultant AuNPs were discrete completely, revealing that the gum could protect Au nanoparticles from aggregation effectively.

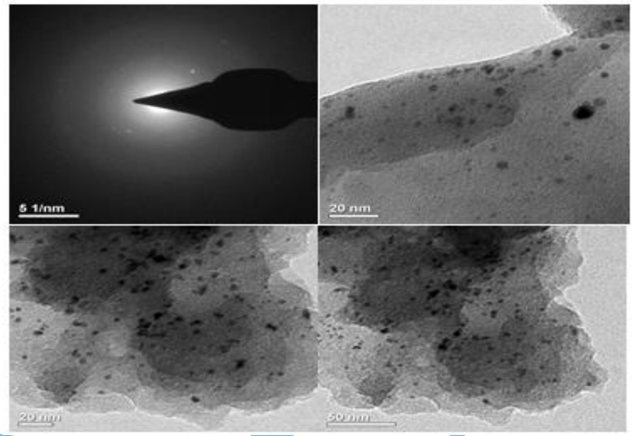

Figure 7: TEM images of platinum nano particles.

4.6 cyclic voltametric analysis:

In cyclic voltammetric analysis the Croton Caudatus Geisel leaf extract free solution makes all the metal ions are reduced to lower oxidation state, since there is no possibility for the formation of NPs. Upon addition of Croton Caudatus Geisel leaf extract in the reaction medium, the cathodic peak shifted towards the negative potential direction, implying that the reduced gold NPs are stabilized by Croton Caudatus Geisel leaf extract (Figure 8). The extent of decrease in anodic peak current is greater than that of the cathodic peak current due to the fact that the rate of reduction of gold ion may be greater than its oxidation. This might be because of the electron donating methoxy, hydroxyl and amine groups containing Croton Caudatus Geisel leaf extract can provide a suitable environment for the formation of nanoparticles. The cyclic voltammogram of AuNPs shows the peaks observed at-0.575 and 0.1V.

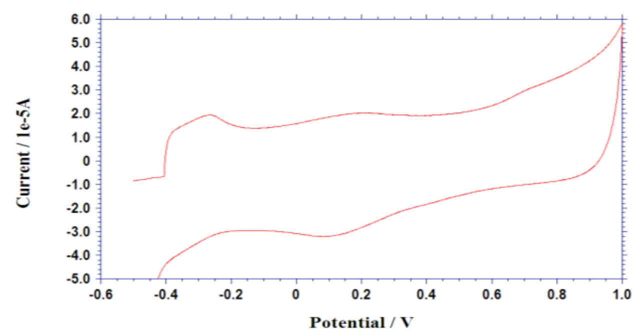

Figure 8: Cyclic voltammograms of platinum nanoparticles

V. CONCLUSION

In conclusion, the Au-NPs were produced by the use of the extract of Croton Caudatus Geisel leaf as reducing and capping agent. In this study, it was observed that the reaction is rapid and is completed within 60 min at 45oC.

We have demonstrated an eco-friendly, rapid green chemistry approach for the synthesis of Pt-NPs using Croton Caudatus Geisel leaf, which provides a simple, cost effective and efficient way for the synthesis of Pt-NPs. Average crystal size calculated from Scherrer equation is found 10 nm for Pt-NPs. The spectroscopic characterizations from UV–Vis, FTIR, TEM and Cyclic voltametry study support the formation and stability of the bio-synthesized Pt-NPs. This simple, efficient and green synthesis of Pt-NPs can be used in various biomedical and biotechnological applications. Therefore, this reaction pathway satisfies all the conditions of a 100 % green chemical process.

VI. ACKNOWLEDGMENTS

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