Catalytic and antibacterial efficacy of biogenic platinum nanoparticles using Cressa cretica leaf broth

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Abstract: Noble-metal nanomaterials are of significant interest today due to their applications in various areas, including bioengineering, industrial, medical applications. In the present study, platinum nanoparticles are synthesized using Cressa cretica leaf broth. The characteristics of biogenic platinum nanoparticles were analysed using UV–Vis spectroscopy, XRD, FT-IR, SEM and EDX techniques. The platinum nanoparticles are rectangular, hexagonal, and pentagonal in shape with the average size of 40-55 nm. The antibacterial efficacy of the biogenic platinum nanoparticles was carried out by disc diffusion assay. It manifested that the platinum nanoparticles were found to be notable inhibition activity against E. coli. The catalytic activity study of reduction of p-nitrophenol showed that the biogenic platinum nanoparticles were highly reactive nanocatalyst in heterogeneous catalysis.

Keywords: Phyto-synthesis, platinum nanoparticles, Catalysis, p-nitrophenol, Antibacterial efficacy

I. INTRODUCTION

In the rapidly emerging field of nanomaterial research, noble metal nanoparticles have entered into a new arena, opening new possibilities in medicine, wastewater treatment [1], catalysis [2] and agriculture [3]. Over the past few decades, there has been an increased concern on metal nanoparticles synthesise due to unique optical and electrical properties [4]. In the process of global efforts to diminish hazardous waste, there is always need to improve a synthesis route which is cheap, cost-effective, non-toxic and productive. Biogenic synthesis of nanoparticles has emerged as an absolute alternative and green approach, making the process cheaper and safer compared to physical& chemical routes [5]. In recent years, metallic nanoparticles, especially gold and platinum nanoparticles were used in the treatment of various disorders such as cancer and cardiovascular diseases (CVD) due to their unique physicochemical and optoelectronic properties [6], [7]. Platinum nanoparticles (Pt NPs) have excellent antimicrobial activities and catalytic activity in 4-nitrophenol reduction [8]-[10].

Various plant parts (leaves, stems, bark, flower and root) have been used as capping and reducing agents in the biogenic synthesis of metal nanoparticles. Several reports are available for biosynthesis of metal nanoparticles using Jasminum auriculatum stem extract [11], Cressa cretica leaf extract [12], rose petals extract [13], Morinda citrifolia root extract [14].

Cress cretica (C. cretica) plants are used in the Indian traditional medicine system. The C. cretica leaves are highly used in the treatment of leprosy, asthma, diabetes, skin diseases and wounds [15]. In the present study, we have evaluated that antibacterial activity and catalytic activity of platinum nanoparticles using C. cretica leaf broth. To the best of our knowledge, this is the first report showing the Catalytic and antibacterial efficacy of platinum nanoparticles using C. cretica leaf broth against human pathogens.

II. MATERIALS AND METHODS

. **Collection of plant materials and preparation of plants leaf broth:**

Cressa cretica plants were gathered from Tuticorin District, Tamilnadu, India. The collected leaves were cleaned and powdered.10g of powdered C. cretica leaves were mixed with 100 ml of distilled water in a 250 ml beaker and heated at 80° C for 30 min. After cooling and filtering through Whatman No.1 paper the leaf broth was stored at 5° C for further analyses.

Synthesis of platinum nanoparticles:

The AR grade Platinum (IV) Chloride was procured from Sigma-Aldrich and the leaf broth used for the reduction of Pt^{4+} ions to Pt^0 at room temperature. In a typical experiment, 10 ml of C. cretica leaf broth was added to 90 ml of 1mM platinum (IV) Chloride solution in a 250 ml beaker. The mixture was stirring under magnetic stirrer for 4 h at the temperature of 50º C. The colour changed from colourless to brownish-yellow, which indicated the formation of platinum nanoparticles.

The resulting solution was purified by repeated centrifugation at 10,000 rpm for 25 minutes to remove any heavy biological materials present in biogenic platinum nanoparticles (Pt NPs). The purified Pt NPs pellets were dried using hot air oven at 60° C for 10 min [16].

Instrumentation:

Platinum (IV) Chloride solution (1mM) showed pH 6.54. C. cretica leaf broth's pH was 9.34. The changed pH of reaction mixtures was measured using digital pH meter (Roy instruments RI 501), during the synthesis of platinum nanoparticles. The biogenic Pt NPs were characterized using UV-Vis spectrophotometer (UV-1800 series) at the range of 200-800 nm. FTIR spectrum of C. cretica leaf broth and the biogenic Pt NPs were recorded on FTIR spectrophotometer (IR Tracer-100 Shimadzu) at the wavelength range of 4000-400 cm^{-1}. Crystallite size and Crystallinity of the biogenic Pt NPs were determined using Bruker X-Ray Diffractometer (D8 Advance ECO XRCD Systems with SSD160 1 D Detector) operated at a voltage of 40 kV. The platinum nanoparticles were characterized with the help of Scanning electron microscopy (Carl Zeiss EVO18) to determine the morphology and size of the nanoparticles. EDX analysis of the biogenic Pt NPs was carried out using Energy dispersive X-ray spectrometer (Quantax 200 with X-Flash-Bruker) to determine the chemical purity and elemental composition of the Pt NPs.

Antibacterial assay:

Agar well diffusion method was followed to determine the antibacterial activity of the biogenic Pt NPs against Escherichia coli and Staphylococcus aureus [17]. Muller-Hinton Agar media plates were swabbed (sterile cotton swabs) with 8 hrs old - broth culture of respective bacteria. After inoculation, wells with the size of 10 mm diameter and about 2 cm a part were made in each of these plates using sterile cork borer. The different concentrations of 10, 20 & 30 µl of the biogenic Pt NPs (100 µg/ml) were added into the wells and allowed to diffuse at room temperature for 2 hrs. The plates were incubated at 37° C for 24 hrs. After incubation, the diameter of the inhibition zone (mm) was measured and the activity index was also calculated.

Catalytic efficacy of Pt NPs:

The catalytic efficacy of the biogenic Pt NPs using C. cretica leaf broth was evaluated using UV–Vis spectrophotometer in the range of 250–600 nm. The catalytic efficacy of the Pt NPs was demonstrated by the reduction of p-nitrophenol to p-aminophenol using sodium borohydride solution [18]. 2 ml of 1.5 mM p-nitrophenol was mixed with 0.5 ml distilled water and 0.5 ml of 10 mM sodium borohydride in a quartz cuvette. Then 0.5 ml (1mg/ml) of the biogenic Pt NPs were added to the above solution in the quartz cuvette. The resulting solution was observed using UV-Vis spectrometry in the range of 250-600 nm at periodic time intervals.

III. RESULTS AND DISCUSSION

Characterization:

The pH of the reaction mixture decreased from 7.14 to 6.54 in presence of C. cretica leaf broth indicating that reduction of platinum chloride solution during the formation of Pt NPs. During the nanoparticles formation, pH of the reaction mixture is reduced.

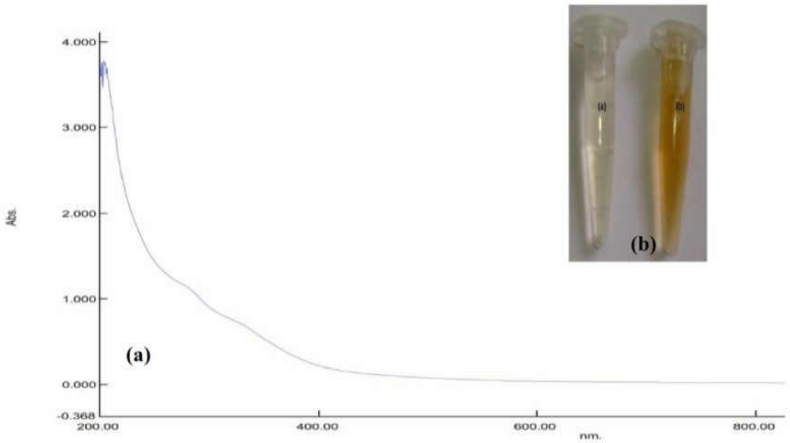

Fig.1 (a) UV-Visible spectra of Pt NPs using *C. cretica* leaf broth (b) Visual analysis of Pt NPs synthesis

The formation of biogenic Pt NPs by the reduction of Pt^{4+} to Pt^{0} with C. Cretica was observed by turning in the colour of reaction mixture from colourless to brownish-yellow (Fig.1(b)). The UV-Vis spectrum of the biogenic Pt NPs using C. cretica leaf broth is presented in Fig.1 (a). The UV-Vis absorption peak is observed at 293 nm due to the synthesis of biogenic platinum nanoparticles. The FT-IR spectra of biogenic Pt NPs using C. cretica leaf broth and C. cretica leaf broth are shown in Fig.2. The FT-IR absorption spectrum of biogenic Pt NPs using C. cretica leaf broth was observed in a range of 628.79 cm^{-1} – 3415.93 cm^{-1}.

The FT-IR spectrum of C. cretica leaf broth was observed in a range of 1560.41 cm^{-1} - 3273.20 cm^{-1}. Based on the variation in the signals of hydroxyl (3273.20 to 3415.93 cm^{-1}), amine (2054 to 2364.73 cm^{-1}) and amide (1631.78 to 1635.64 cm^{-1}) groups of C. cretica leaf broth are contributed to the formation and stabilization of the biogenic Pt NPs.

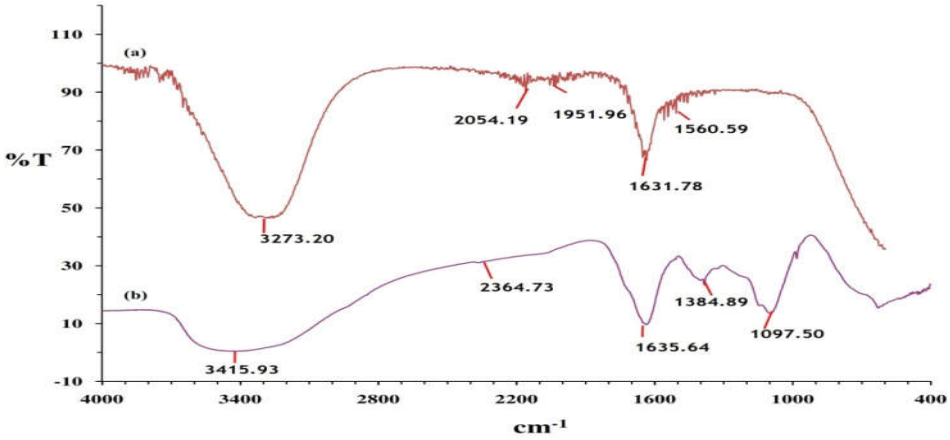

Fig.2 FT-IR spectra of (a) *C. cretica* leaf broth (b) Pt NPs using *C. cretica* leaf broth

Furthermore, two peaks were observed at 1384.89 cm^{-1} and 1097.50 cm^{-1} in the platinum nanoparticles, corresponding to nitro groups and ketone groups respectively. The appearance of these two peaks in the Pt NPs implied that formation of nitro groups from the amide groups, and conversion of the alcoholic group into ketone group. The functional groups are more characteristic of flavonoids, steroids, phenolic compounds, and amino acids which are rich in C. cretica leaves broth [15]. FT-IR results indicate that the flavonoids, steroids, phenolic compounds, and amino acids present in the C. cretica leaf broth are involved in the reduction of platinum ions and are adsorbed on the surface of the biogenic platinum nanoparticles.

The XRD peaks at 39.7°, 46.32°, 67.4° and 81.2° can be indexed to the (111), (200), (220) and (311) plane of ffc of metallic platinum respectively (JCPDS 00-04-0802). The XRD Pattern (Fig.3 (a)) shows the strong and narrow diffraction peaks revealed that the biogenic Pt NPs are crystalline in nature [16], [19]. The average crystallite size of the biogenic Pt NPs was estimated using the Debye–Scherrer's formula and is 40-60 nm.

EDX image displayed (Fig.3 (b)) that the characteristic of platinum peaks and other peaks (Mavukkandy et al., 2016; Song et al., 2010). It exhibits the successful formation of the biogenic Pt NPs using C. cretica leaf broth. The other peaks for O, S, Cl, K & Mg were observed, which originated from biomolecules present in C. cretica leaf broth.

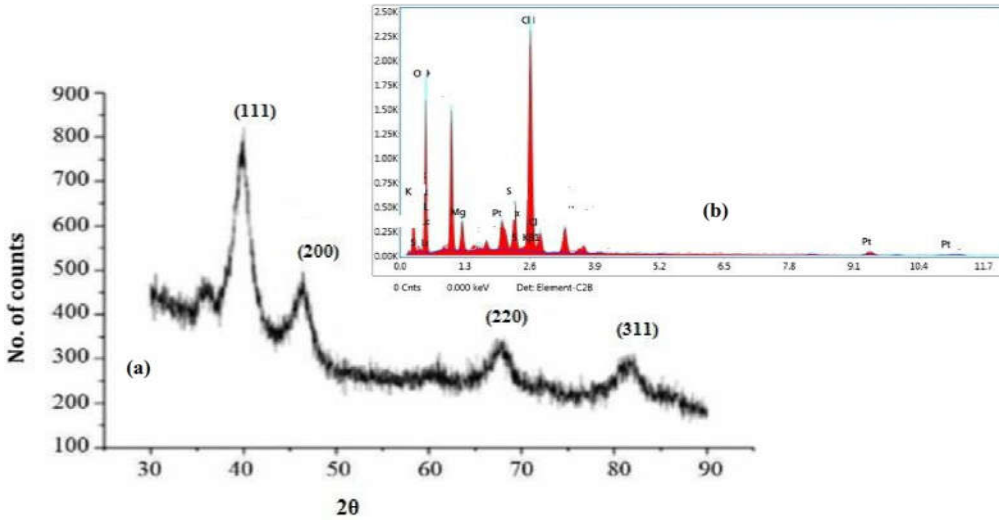

Fig.3 (a) XRD patterns of Pt NPs *C. cretica* leaf broth (b) EDX image of Pt NPs using *C. cretica* leaf broth

The SEM images (Fig. 4) exhibit that the biogenic Pt NPs are rectangular, hexagonal, and pentagonal with 40-55 nm in size. The deviation in size and shape of the biogenic Pt NPs occurs, due to the different growth phases of platinum nanoparticles [20].

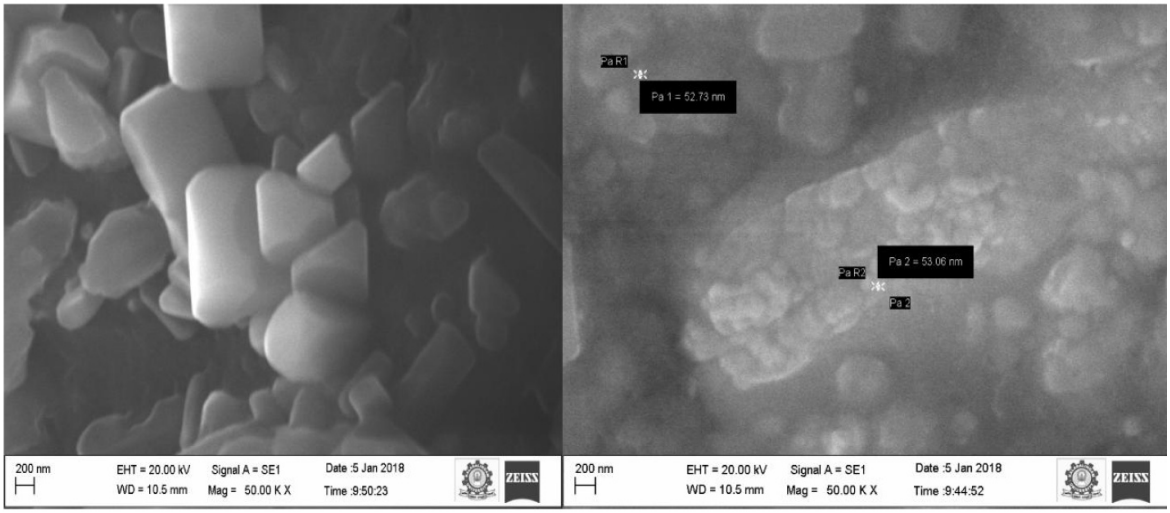

Fig.4 SEM images of Pt NPs using *C. cretica* leaf broth at different magnification

Antibacterial efficacy of Pt NPs:

The antibacterial efficacy of the biogenic Pt NPs using C. cretica leaf broth was probed by disc diffusion assay and presented in Fig.5 & Table.1. The zone of inhibition of the biogenic Pt NPs (30 µl) was 1 for Staphylococcus aureus, 3 mm for E. coli. This present study reveals that the biogenic Pt NPs from C. cretica have better inhibition activity against E. coli than S. aureus (Ahmed et al., 2016) due to the cell membranes of gram-negative bacteria are made up thin layers of peptidoglycan than that of gram-positive bacteria. The biogenic platinum nanoparticles exhibit notable inhibition efficacy against proliferation of E. coli.

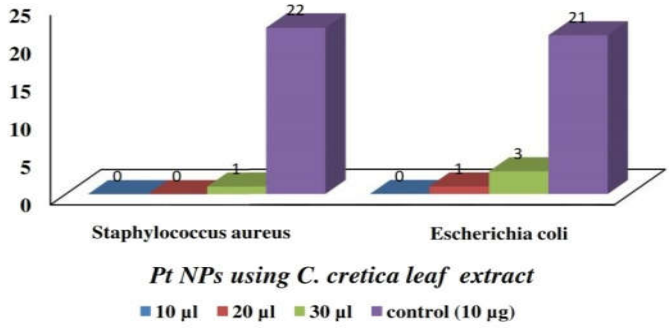

Fig.5 Antibacterial activity of biogenic Pt NPs using *C. cretica* leaf broth

Table.1 Zone of inhibition (mm) of biogenic Pt NPs using *C. cretica* leaf broth against human pathogenic bacteria

S.No	Pathogenic bacteria	Zone of inhibition in diameter (mm)			
		concentration µg/ml			Standard (Gentamicin) 10 µg
		10 µl	20 µl	30 µl	
1.	Staphylococcus aureus	0	0	1	22
2.	Escherichia coli	0	1	3	21

Catalytic activity of Pt NPs:

The catalytic activity of the biogenic Pt NPs was observed using UV-Vis spectra in the range of 250-600 nm. Reduction of p-nitrophenol was observed by reduction of the absorption signal at 400 nm and by development and rising of the signal at 300 nm, indicating the formation of p-aminophenol (Fig.6) [13, 43]. The reduction reaction was completed within 30 minutes. The platinum nanoparticles act as electron transfer mediator in the reduction reaction. The rate of reaction depends on the size of the nanoparticles, indicating small-sized platinum nanoparticles should have the highest catalytic activity.

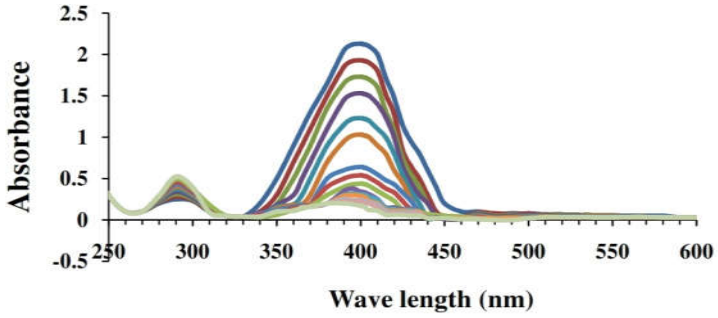

Fig.6 Catalytic activity of phyto-synthesized Pt NPs using *C. cretica* leaf extract in 4-nitrophenol reduction

IV. CONCLUSION

In this present investigation, we have demonstrated a simple and eco-friendly method to directly fabricate platinum nanoparticles using C. cretica leaf broth. SEM studies exhibited that the biogenic Pt NPs are rectangular, hexagonal, and pentagonal with diameter of 40-55 nm. The XRD analysis confirmed that the biogenic nanoparticles are in crystalline nature. The EDX result confirmed the formation of the Pt NPs. The biogenic Pt NPs have notable inhibition activity against human pathogenic bacteria and have greater catalytic efficacy in p-nitrophenol reduction. Thus the biogenic Pt NPs can be used as wide applications in environmental concern, various industrial and medical applications.

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