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Biofabrication, characterization, and possible bio-reduction mechanism of platinum nanoparticles mediated by agro-industrial waste and their catalytic activity

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ABSTRACT

The present study showed biofabrication of platinum nanoparticles (Pt-NPs) using agro-industrial waste *Punica granatum*'s peel extract. Appearance of the broad spectrum from visible to the ultraviolet region, confirmed the biofabrication of Pt-NPs. Pt-NPs were spherical, within size range of 16–23 nm. XRD suggested the fabrication of crystalline Pt-NPs with (111) plane in predominant orientation. The negative ζ potential value of colloidal Pt-NPs revealed high stability. FTIR confirmed the role of hydroxyl and carbonyl groups of polyphenolic compounds of peel extract for biofabrication. The reduction of anthropogenic pollutant, 3-nitrophenol, by $NaBH_4$ using colloidal Pt-NPs established it as an efficient "green catalyst."

Introduction

Today, transition metal nanoparticles, particularly platinum nanoparticles (Pt-NPs) are subject to intensive research. The emerging catalytic applications of Pt-NPs in variety of reactions such as hydrogenation [1], oxidation [2], reduction [3], and for the synthesis of organic dyes [4] has attracted the focus of researchers. The biofabricated nanoparticles for their eco-friendly properties are the preferred option for variety of applications. The development of simple and environment-friendly methods for controlled synthesis of Pt-NPs is therefore, important, not only for the fascinating utilization of Pt-NPs but also for the demands of green chemistry.

In recent years, significant efforts have been made toward fabrication of nanoparticles using biogenic resources, which also represents a growing connection between biotechnology and nanotechnology [5]. This approach for nanoparticle fabrication shows several benefits concerning biocompatibility, thermal and chemical stability, high efficiency, fast process, cost efficiency, and eco-friendly nature [6,7]. However, till date plant-based synthesis of Pt-NPs has been reported only by leaf extract of *Ocimum sanctum* [8], *Diospyros kaki* [9], *Cacumen platycladi* [10], and *Anacardium occidentale* [11]. Few other biological resources are also reported for biological synthesis of Pt-NPs such as horse spleen apoferritin [12] and honey [4].

Recently, use of *Punica granatum* (*P. granatum*) peel has been reported for cost-effective and environmentally benign synthesis of Ag [13] and Au-NPs [14]. Earlier, leaf [15] and fruit [16] of *P. granatum* were also utilized for biofabrication of Au and Ag-NPs. *P. granatum* peel is one of the most valuable by-products of the food and agriculture industry, which is mainly composed of ellagic tannins, punicalagin, gallic acid, ellagic acid, and quercetin [17,18]. It is also shown antioxidant [19,20], antimutagenic [21], and chemo-preventive potential [22]. An extensive literature survey revealed that there is no report available for the biosynthesis of Pt-NPs using *P. granatum* peel. In the present study, antioxidant potential of *P. granatum* peel is utilized for biofabrication of Pt-NPs.

The present study involves biofabrication of Pt-NPs using agro-industrial waste *P. granatum* peel as the bio-reducing agent. Further, catalytic activity of biofabricated colloidal Pt-NPs is also investigated for reduction of anthropogenic pollutant 3-nitrophenol (3-NP) using sodium borohydride ($NaBH_4$) as a hydrogen or electron donor. Nowadays, nitrophenols are extensively used as raw materials in pharmaceutical, dye, and insecticide industries [23]. Since nitrophenols are readily soluble and stable in water [24] they are abundantly present in agricultural and industrial waste water. Further, they are perilous to public

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health as they possess mutagenic and carcinogenic properties harmful for humans [25]. It is therefore, necessary to eliminate nitrophenols from industrial waste water. The reduction of 3-NP to 3-aminophenol (3-AP) is therefore, of significant importance. Use of eco-friendly biofabricated colloidal Pt-NPs as a catalyst in this direction is of enormous value in environmental and industrial aspect. Biofabricated Pt-NPs are characterized by UV–visible spectrophotometer (UV–visible), dynamic light scattering (DLS), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FTIR) techniques. Further, the reduction of 3-NP is monitored by UV–visible spectrophotometer.

Experimental

Materials

Chemicals, including hexachloroplatinic acid ($H_2PtCl_6.6H_2O$) 99.9%, 3-nitrophenol ($C_6H_5NO_3$) 98%, and sodium borohydride ($NaBH_4$) 98% were procured from HiMedia Pvt. Ltd, Mumbai, India. Peels of the *P. granatum* fruit were collected from the local market of Surat, Gujarat, India. Double-sterilized Milli-Q water was used throughout the experiments.

Preparation of the P. granatum *peel extract and biofabrication of colloidal Pt-NPs*

A total of 30 g of fresh peel of *P. granatum* was extracted with 120 mL of distilled water at 60 °C for 10 min and filtered. The solution was decanted and stored at 4 °C for further use. About 100 mL of aqueous *P. granatum* peel extract was added to 400 mL of 1×10^{-3} M $H_2PtCl_6.6H_2O$ solution. The mixture was maintained at 90 °C in a sealed flask for 30 min under shaking conditions on a rotary shaker (500 rpm). The reduced Pt-NPs were sonicated for 10 min to separate Pt-NPs from the biomolecules present in *P. granatum* peel extract. After sonication, Pt-NPs were purified by repeated centrifugation at 14,000 rpm for 10 min and the pellets were washed thrice with distilled water to remove the impurities. Control reactions, in which $H_2PtCl_6.6H_2O$ solution and peel extract was kept in a separate conical flask, under the same reaction conditions.

Evaluation of catalytic activity of biofabricated colloidal Pt-NPs

In order to find out the catalytic activity of biofabricated colloidal Pt-NPs (Pt-NPs dispersed in *P. granatum* peel extract) three typical reactions were carried. In the first reaction, 1 mL of 1×10^{-3} M 3-NP was mixed with 0.5 mL of water. In the second reaction, 0.5 mL of 1 M $NaBH_4$ was added to the first reaction mixture. In the third reaction, 1 mL of colloidal Pt-NPs was mixed with reaction mixture obtained from the second reaction. All the three reactions were monitored by UV–visible spectrophotometer (DR 5000, HACH, USA). Temperature and concentration dependent catalytic activity of biofabricated colloidal Pt-NPs were also carried out for 3-NP reduction. Catalytic activity of *P. granatum* peel extract and bulk $H_2PtCl_6.6H_2O$ was also evaluated for 3-NP reduction.

Characterization of Pt-NPs

Biofabrication of Pt-NPs was monitored first by visual inspection and then by using UV–visible spectrophotometer (DR 5000, HACH, USA). Baseline correction was made with *P. granatum* peel extract. Hydrodynamic size distribution and ζ potential of the colloidal Pt-NPs were determined by using DLS (Zetasizer Nano ZS90, Malvern, UK). TEM and selected area electron diffraction (SAED) pattern data were obtained by using TEM (CM-200, Philips, UK). TEM image was recorded at 100 kV accelerating voltage with resolution of 2.4 Å. XRD pattern of Pt-NPs on the glass substrate was recorded by using XRD (X'Pert Pro, PANalytical, Holland) operated at a voltage of 45 kV and current of 35 mA with Cu–Kα radiation (K = 1.5406 Å). The scanning range (2θ) was selected from 20 ° to 80 ° at 0.045 °/min continuous speed. The crystallite size of the Pt-NPs was calculated using Scherrer's formula. The natures of elements were identified by EDX (INCA X-sight, Oxford Instruments, UK) coupled with scanning electron microscopy (SEM) (JSM-6380LV, JEOL, Japan). In order to identify the phytochemicals responsible for bio-reduction and stabilization of Pt-NPs, FTIR analysis of peel extract before and after bio-reduction and biogenic Pt-NPs were carried out using FTIR (Magna-550, Nicolet, USA). All spectra was taken in the mid-IR region of 600–3600 cm^{-1}.

Results and discussion

UV–visible spectroscopy analysis for biofabrication of Pt-NPs

The biofabrication of colloidal Pt-NPs was confirmed by UV–visible spectroscopy analysis. The $H_2PtCl_6.6H_2O$ solution (pale yellow) showed an absorption peak at around 260 nm in its UV–visible spectrum due to the ligand-to-metal charge-transfer transition between Pt^{4+} and Cl^- ions [26], displayed in Fig. 1. As the bio-reduction reaction was carried out, colloidal Pt-NPs were formed simultaneously with a change in pale yellow color of $H_2PtCl_6.6H_2O$ solution into light brown. The absorption peak present at 260 nm disappeared and was replaced by a broad continuous absorption spectrum, which gradually increases in intensity from visible to the ultraviolet region, suggested Pt^{4+} ions were completely reduced to Pt^0 [27]. Control reaction mixture recovered as pale yellow in color, with no light-brown, being observed suggested Pt-NPs were formed only in presence of *P. granatum* peel extract.

DLS and ζ potential analysis

Fig. 2a revealed that the *Z*-average diameter of the biofabricated Pt-NPs was 30 nm with a polydispersity index (PDI) 0.270. The corresponding average ζ potential value of −15.7 mV confirmed the stability of Pt-NPs in colloidal solution (Fig. 2b). This low value of ζ potential of biofabricated nanoparticles was attributed to the additional influence by the electric charge of bio-organics present in peel extract. Various process parameters such as biomaterial dosage, temperature, and pH (change the electric charge of bio-organics), which might further affect their capping and stabilizing

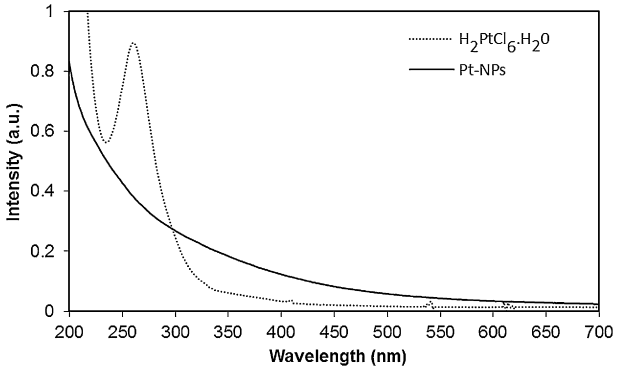

Fig. 1. UV–visible spectra of aqueous $H_2PtCl_6.6H_2O$ and colloidal Pt-NPs.