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Catalytic degradation of anthropogenic dye pollutants using palladium nanoparticles synthesized by gum olibanum, a glucuronoarabinogalactan biopolymer

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ABSTRACT

An eco-friendly, facile, single pot green method for the synthesis of palladium nanoparticles from palladium chloride was developed using non-toxic, renewable, glucuronoarabinogalactan polymer; gum olibanum (*Boswellia serrata*), as a dual functional reductant and stabilizer. UV–vis spectroscopy (UV–vis), dynamic light scattering (DLS), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) techniques were used to characterize the generated nanoparticles. The palladium nanoparticles formation was evidenced from the appearance of intense brown colour and broad continuous absorption spectra in the UV–vis region.The produced nanoparticles were spherical, polydisperse, ranged from 2.5–8.8 nm and the average particle size was about 6.6 ± 1.5 nm. The selected-area electron diffraction and XRD patterns established the face centred cubic crystal structure of the fabricated nanoparticles. The IR spectra elucidated the association of hydroxyl, carboxylate groups and proteins of the gum in the reduction and capping of the nanoparticles. The biogenic nanoparticles were non-toxic to both Gram-positive and Gram-negative bacteria even at higher loadings and exhibited efficient antioxidant activity. The homogeneous catalytic activity of palladium nanoparticles was studied by probing the reduction of synthetic dyes such as coomassie brilliant blue G-250, rhodamine B, methylene blue and 4-nitrophenol with sodium borohydride. The nanoparticles exhibited excellent dye degradation activity and the results demonstrate the possible application of biogenic palladium nanoparticles as nanocatalyst in eco-friendly environmental remediation of waste waters polluted with toxic, mutagenic, hazardous dyes and pigments.

1. Introduction

Several man-made chemical dyes are widely used in various industries including textile, printing, photography leather, pharmaceutical, cosmetic, ceramic and food processing. For example, coomassie brilliant blue G-250 is a protein staining dye used widely for visualizing proteins after electrophoretic separation and for protein quantification by Bradford assay (Rauf et al., 2005). Methylene blue is thiazine dye used for staining body fluids and tissues during surgery and diagnostic exam. Also utilized in the trace level estimation of sulphide ions in waters and applied as an anti-malarial agent, chemotherapeutic agent in aqua culture. The reduction of methylene blue is finding applications in various fields including textile industry, data storage media, holographic industry etc (Meena Kumari and Philip, 2013). Rhodamine B is a fluorescent staining dye which is extensively used in florescence microscopy, flow cytometry, ELISA tracer and also utilized as a tracer for determining the flow direction and transport of water (Cheng et al., 2010). 4-nitrophenol is a carcinogenic, mutagenic and cyto-toxic and embryonic-toxic agent, used extensively in the manufacturing of drugs, insecticides, fungicides, explosives and dyes. It is also listed by the United States Environmental Protection Agency as one of the most common hazardous and toxic organic pollutants in industrial and agricultural waste waters and a strong skin irritant and acute exposure in humans causes headaches and cyanosis (Narayanan et al., 2013).

All these industries demand enormous quantity of water at various stages and also generate effluents enriched with different dyes (Junejo et al., 2014). These industrial effluents with anthropogenic pollutants lead to high biological oxygen demand and chemical oxygen demand and also prevent photosynthesis of aqueous flora.

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Most of these dyes are mutagenic, teratogenic and carcinogenic and pose high toxicity towards native flora and fauna of the environment and including human beings (Alqaragully, 2014). Thus, the consequence necessitates the development of methods for degradation of synthetic dyes. Common techniques such as adsorption, coagulation, flocculation, oxidation, chemical precipitation etc are used for removal of dyes. Recently, nanoparticles of noble metals have gained importance in reduction and degradation of dyes due to their stability and high catalytic activity (Junejo et al., 2014). The catalytic activity of different metallic nanoparticles such as silver, gold, copper, palladium and platinum was studied in detoxification of various dyes (Ashokkumar et al., 2013; Junejo et al., 2014; Narayanan et al., 2013; Nemanashi and Meijboom, 2013; Pandey and Mishra, 2014; Qian et al., 2014; Suvith and Philip, 2014). Various biosynthetic routes have been reported for the synthesis of silver, gold, copper, palladium and platinum using natural reductants including *Gloriosa superba* leaf extract (Ashokkumar et al., 2013), guar gum (Pandey and Mishra, 2014), *Cylindrocladium floridanum* fungus (Narayanan et al., 2013), coconut oil (Meena Kumari and Philip, 2013), *Catharanthus roseus* leaf extract (Kalaiselvi et al., 2015), *Anacardium occidentale* dried leaf (Sheny et al., 2012), tannic acid (Meena Kumari et al., 2013) etc.

In an earlier study by us, we have reported the silver nanoparticle synthesis with gum olibanum by virtue of its natural abundance, non-toxic, low cost and medicinal values (Kora et al., 2012). Gum olibanum is a natural oleoresin gum exudate from the bark of *Boswellia serrata* (Burseraceae family), a native tree of India. It is commonly known as *Salai guggul* and produced in the states of Madhya Pradesh, Andhra Pradesh, Rajasthan, Gujarat, Maharashtra, Bihar, Odisha and Assam. This multipurpose aromatic is exploited in food, pharmaceuticals, paints, ceramics and textile industries. The gum possess broad spectrum of properties and utilized for the management of several inflammatory, arthritic, pulmonary and intestinal disorders in Ayurvedic and Unani medicine (Shukla et al., 2005; Upaganlawar and Ghule, 2009). Characteristically the gum olibanum consists of essential oil, water soluble gum (polysaccharides), resin and insoluble matter. The major polysaccharide is 4-*O*-methyl-glucuronoarabinogalactan, abundant in neutral sugars and composed of galactose, arabinose, xylose and glucuronic acid (Sen et al., 1992). In this scenario, we have developed eco-friendly, facile, single pot green method for the synthesis of palladium nanoparticles from palladium chloride using renewable, glucuronoarabinogalactan type of Indian gum: gum olibanum as both the reducing and stabilizing agent.

In this study, we have characterized gum olibanum synthesized palladium nanoparticles with various techniques for UV–vis absorption, hydrodynamic diameter, particle morphology, size, crystal structure etc. We have evaluated the homogeneous catalytic activity of the produced green palladium nanoparticles via borohydride reduction by choosing four typical dyes; coomassie brilliant blue G-250, methylene blue, rhodamine B and 4-nitrophenol. The nanoparticles were also investigated for their antioxidant and antibacterial activities.

2. Experimental

2.1. Synthesis of palladium nanoparticles

Palladium chloride ($PdCl_2$) of analytical reagent grade was used for synthesis. All the solutions were prepared in ultra pure water. "Gum olibanum", grade-1 was purchased from Girijan Co-operative Corporation Ltd., Hyderabad, India. The gum was powdered in a Prestige Deluxe–Vs high speed mechanical blender (Bengaluru, India) and sieved to obtain a particle size of 38 μm. Then, a 0.5% (w/v) of homogeneous gum stock solution was prepared in ultra-pure water by stirring overnight at room temperature. Then, this solution was centrifuged (5500 × *g*, 10 min) to remove the insoluble materials and the supernatant was used for synthesis (Fig. 1). The palladium nanoparticles were synthesized by autoclaving the gum solutions containing $PdCl_2$ at 121 °C and 103 kPa for 30 min. The effect of variations of concentrations of gum (0.1–0.5%) and palladium chloride (0.125–1.0 mM) on nanoparticle synthesis was also studied.

2.2. Characterization of synthesized palladium nanoparticles

The UV–vis absorption spectra of the prepared palladium nanoparticle suspensions were recorded using Biotek Synergy™ H1 microplate reader (Winooski, Vermont, USA), from 300 to 800 nm. The autoclaved gum solutions were used as reference blank. The *z*-average particle size, polydispersity index (PDI) and zeta potential of the produced palladium nanoparticles were assessed with a Malvern Zetasizer Nano ZS90 (Malvern, UK). The size and shape of the nanoparticles were obtained with FEI Tecnai 20 G2 S-Twin (Eindhoven, Netherlands) transmission electron microscope (TEM), operating at 200 kV. The samples for TEM were prepared by depositing a drop of colloidal suspension on a carbon coated copper grid and drying at room temperature. The X-ray diffraction analysis was conducted with a Rigaku, Ultima IV diffractometer (Tokyo, Japan) using monochromatic Cu Kα radiation (λ = 1.5406 Å) running at 40 kV and 30 mA. The intensity data for the nanoparticle suspension deposited on a glass slide was collected over a 2θ range of 30–100° with a scan rate of 1°/min. The nanoparticles were recovered from the synthesized solutions by centrifugation and made into powders using an FTS Systems, Dura–Dry™ MP freeze dryer (New York, USA). The IR spectra of the lyophilized samples were recorded using Bruker Optics, TENSOR 27 FTIR spectrometer (Ettlingen, Germany); over a spectral range of 1000–4000 cm^{-1}.

2.3. Catalytic activity of synthesized palladium nanoparticles

The catalytic activity of palladium nanoparticles at an optimum concentration of 3.2 μg/mL (0.75 mM–40 μL) was determined by studying the reduction of four chemical dyes; coomassie brilliant blue G-250 (CBB), methylene blue (MB), rhodamine B (RB) and 4-nitrophenol (4-NP), with sodium borohydride ($NaBH_4$) at 12.5 mM concentration (500 mM–25 μL), as a model reaction (Kalaiselvi et al., 2015). $NaBH_4$, CBB, MB, RB and 4-NP of analytical reagent grade were used. The dye degradation was investigated by measuring the UV–vis spectra for 2 min. The control reactions were monitored in the absence of $NaBH_4$ and palladium nanoparticles. The negative control was also included with autoclaved gum and $NaBH_4$ solutions.

2.4. Antibacterial activity of synthesized palladium nanoparticles

Staphylococcus aureus (ATCC 25923) and *Pseudomonas aeruginosa* (ATCC 27853) were used as test strains representing Gram-positive and Gram-negative bacteria, respectively. The bacterial suspension was prepared from overnight grown culture in nutrient broth by adjusting the turbidity to 0.5 McFarland standard.

2.4.1. Well diffusion assay

The antibacterial activity of the synthesized nanoparticles was determined with well diffusion method, a solid agar assay (Kora et al., 2010). Mueller Hinton agar plates were inoculated with turbidity adjusted bacterial suspension and aliquots of nanoparticle suspension containing 5 μg (0.75 mM–62.5 μL), 10 μg (0.75 mM–125 μL) and 20 μg (0.75 mM–250 μL) of palladium were