Journal of Photochemistry & Photobiology, B: Biology 165 (2016) 87–95

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology, B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

Biosynthesis of palladium nanoparticles by using *Moringa oleifera* flower extract and their catalytic and biological properties

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ARTICLE INFO

Article history:
Received 31 July 2016
Accepted 28 September 2016
Available online 29 September 2016

Keywords:
Moringa oleifera
p-Nitrophenol
PdNPs
A549 cells
Suzuki reaction

ABSTRACT

The biosynthesis of nanostructured biopalladium nanoparticles (PdNPs) from an aqueous solution of crystalline palladium acetate is reported. For the synthesised PdNPs in solution, an agroforest biomass waste petal of *Moringa oleifera* derived bis-phthalate was used as natural reducing and biocapping agents. Continuous absorption in the UV region and subsequent brown colour change confirmed the formation of PdNPs. A strong surface plasmon peak for PdNPs occurred at 460 nm. PdNPs were characterized by SEM with EDX, FTIR, TEM and DLS. The chemical composition of the aqueous extract was determined by GC–MS coupled with FTIR and ^{1}NMR. The catalytic degradation effect by PdNPs on industrial organic toxic effluents p-nitrophenol (PNP) and methylene blue dye was monitored by UV Spectroscopy. On the other hand PdNPs catalysed the base mediated suzuki coupling reaction for biphenyl synthesis, in water. Moreover, PdNPs were found to be reusable catalysts. Toxicity studies of PdNPs showed that the death of brine shrimp to be <50%. Therefore, PdNPs displayed potential for further anticancer studies via tumour cell lines. The in vitro cytotoxicity evaluation of the extract capped nanoparticles was carried out using human lung carcinoma cells (A549) and peripheral lymphocytes normal cells by MTT cell viability assay. Also, PdNPs showed antibacterial activity against *Enterococcus faecalis* among the different tested strains, including *Bacillus cereus*, *Staphylococcus aureus*, *Esherichia coli* and *Candida albicans*, *Candida utilis*.

1. Introduction

Agroforestry waste can have serious environmental impacts, as some wastes will eventually rot or burn to produce heat however, barely utilized [1–6]. The recognition of agricultural waste and forestry residues at the nanoscale can create a new market for farmers and other independent craftsmen who possess stockpiles of agricultural waste as a by-product of their trade. Farmers can generate revenue for themselves while providing a greener and sustainable form of technology. Currently, the rapid expansion of the nanotechnology industry is prompting the need to investigate the toxic effects of nano-sized particles (NPs) and its potential for improving the environment, betterment of human health and development of industrial/biological products [7–12]. Such knowledge creates a platform for nanotechnology to grow in a responsible and sustainable manner. The synthetic chemicals, namely, p-nitrophenol (PNP) and methylene blue (MB) are used as a starting material to manufacture textiles, pharmaceuticals, and cosmetics products; hence it is widely distributed in the environment. Since PNP is toxic, biohazardous and may accumulate in the food chain, it poses detrimental health and environmental risks. Further, p-nitrophenol is also regarded as a major risk pollutant by the US Environmental Protection Agency [13]. Acute inhalation or ingestion of p-nitrophenol in humans causes severe headaches, drowsiness, cyanosis, nausea and vomiting. Whereas, basic dyes such as MB are reported to cause allergic dermatitis, cancer and mutations [14]. Contact with eyes causes irritation in humans. One of the major problems concerning textile waste water is the disposal of dye effluent [15]. Therefore, removal of dyes from the effluent is the responsibility of textile units before its final discharge.

Nanocatalysis is a recent important technology leading to the total mineralization of most organic effluents [16]. The metal nanoparticles Ag, Pt, Au and Pd have provided numerous applications in heterogeneous and homogeneous catalytic reactions [17]. The use of renewable, non-toxic solvents that are inexpensive and environmentally benign is an important green strategy implemented for the one-step green synthesis of monodispersed Pd nanocrystals. The Akira suzuki cross coupling reaction has been used to synthesize intermediate compounds for industrial raw materials [18–21].

The Moringa (*Moringa oleifera Lam.*) is one source of these type of natural remedies. *Moringa olifera*, *Moringa peregrine* and *Moringa ovalifolia* commonly called "African Moringa" are large trees indigenous to southern part of South Africa. Root-bark extracts are used as anthelmintic, analgesic and astringent for treatment of ulcers, tumours, ear ache, and tuberculous glands in the neck [22–26]. Moringa leaves has

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http://dx.doi.org/10.1016/j.jphotobiol.2016.09.039
1011-1344/

been of interest to researchers because of their use as traditional medicine in the treatment of various diseases in Asia and Africa. Recently, African countries, including South Africa started cultivating moringa [27] for use as traditional medicine for both humans and animals [28]. Moringa tree itself represents an important resource for health care products. Almost all plant parts are used in traditional phytomedicine and as vegetables for dietary purposes [29]. Elevated nutrient content in their leaves can partly be attributed to the relatively low moisture content (ca. 76%) of fresh leaves compared with ca. 90% moisture content of most vegetables. Moringa leaves contain approximately 27% protein by dry weight and all essential amino acids. In addition, they contain high levels of vitamins and beneficial phytoactives [30–31].

The present study describes the in vitro one step facile assembly of PdNPs using *Moringa oleifera* flower, morphological and stability elucidation, its catalytic degradation of p-nitrophenol, methylene blue, and reductive elimination Suzuki reaction. Furthermore, toxicity assessment on the brine shrimp larvae (*Artemia salina*) is described, cytotoxic effects on the cancer cell line and the effects on healthy lymphocytes are elucidated. The antimicrobial activity of nanostructured bio palladium (PdNPs) was observed against all four bacterial and two yeast strains using a well diffusion assay [35]. The aqueous extract prepared from *Moringa oleifera* was used for the rapid synthesis of PdNPs, which is very simple and eco-friendly in nature. The results of the present findings fortify the potential of the biosynthesized PdNPs as a resource for the discovery of multi-application like anticancer, antimicrobial, antioxidant agent, safety assay, and biocatalytic activity.

2. Materials and Methods

2.1. Preparation of Palladium Nanoparticles (PdNPs)

The *Moringa oleifera flower* was collected from the durban agricultural farm and identified at the Natal Herbarium. All reagents were obtained from Sigma-Aldrich and used without further purification. The synthesis can be summarized as follows: Flower were dried for few days at dark room. The flower solution was prepared by weighing 10 g of fine flower powder in a 250 mL Erlenmeyer flask along with 100 mL of double distilled water and then boiling the phyto-mixture for 20 min, cooled and stored at room temperature; this concoction was used within a week. Water extracts of *Moringa oleifera* were added into conical flasks containing 1 mM palladium acetate solution. The formation of palladium nanoparticles was monitor by the improvement of light yellow colour which is a characteristic of PdNPs (see Figs. 5 and 9).

2.2. Characterization of Palladium Nanoparticles

2.2.1. UV–Vis Absorption Spectroscopy

UV–Vis spectra were recorded as a function of the reaction; the intensity steadily increased to saturation as a function of the reaction time. The colour change from dark brown to light yellow is due to the excitation of surface plasmon resonance (SPR) in the palladium nanoparticles. The optical properties of PdNPs were monitored by UV–vis absorption spectroscopy using a Varian Cary-50.

2.2.2. Zeta Potential and Particle Size Distribution

The zeta potential of PdNPs was evaluated using a Zetasizer Nano ZS (Malvern Instruments Inc., USA). This equipment was also employed to determine the particle size and stability of the particles.

2.2.3. Transmission Electron Microscopy (TEM)

The PdNPs shape, morphology and size distribution was evaluated by a Transmission Electron Microscope (JEOL 1010 TEM using a Mega view III camera and iTEM software). One drop of PdNP suspension was added on a carbon coated copper grid. The program ImageJ was used to determine the size of PdNPs from TEM images.

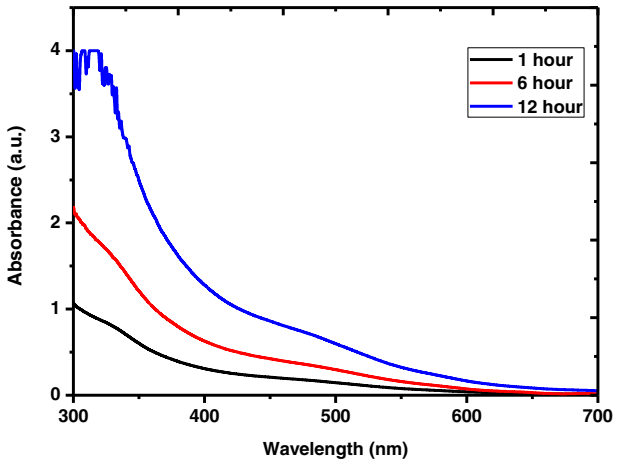

Fig. 1. UV–vis absorption spectra of PdNPs at different reaction times.

2.2.4. Scanning Electron Microscopy (SEM)

The PdNPs was characterized using SEM/EDX (Carl Zeiss Ultra Plus scanning electron microscope) techniques. The crystalline nature, size were confirmed by SEM microscopy and the EDX pattern for PdNPs showed signals for palladium metal.

2.2.5. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR (Varian 800 FTIR spectrophotometer) of as-synthesized PdNPS compared with flower aqueous extract. Both PdNPs and flower extracts displayed absorption bands: whereas PdNPs assigned as antisymmetric and symmetric stretching frequencies.

2.2.6. TGA/DSC

Nanoparticles thermal stability determine by Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) were performed on a SDT Q600 V20.9 build 20 under flowing N2 at a ramp rate of 20 °C per minute to 700 °C.

2.3. Catalytic Reduction of Methylene Blue (MB)

An aqueous ice cold solution of $NaBH_4$ (0.5 mL of 0.1 M) was mixed with an aqueous stock solution of methylene blue (2 mL, 10–5 M) in a standard quartz cuvette and PdNPs (25 μL) was added. The final volume was adjusted with Millipore water to get the final volume as 3 mL. The mixture was shaken well and the reaction was monitored with the help of a UV–vis spectrophotometer in the scanning range of 300 to 700 nm at room temperature.

2.4. Catalytic Reduction of P-Nitrophenol (PNP)

Chilled aqueous solution of sodium borohydride (1 mL, 15 mM) was mixed with P-nitrophenol (1.7 mL, 0.2 mM) in a standard quartz cuvette. The yellow colour of the P-nitrophenol changed yellowish brown due to the intermediate formation of the 4-nitrophenolate ion. An aliquot of PdNPs prepared at room temperature (0.4 mL) was added to the resulting solution, and the time-dependent absorbance spectra peak was recorded. The maximum scanning range 250 nm to 750 nm at room temperature.

2.5. Suzuki Reaction in Water

To a 10 mL flask, a mixture of iodobenzene (0.6 mmol, 0.067 mL), phenylboronic acid (0.5 mmol, 0.6 g) and K_2CO_3 (1.75 mmol, 0.24 g) was added to cold water (1.5 mL) and additive PEG-300 (1.5 mL). 1 mL PdNPs was added as a catalyst. The homogenous mixture was