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Green-synthesized gold nanoparticles from *Plumeria alba* flower extract to augment catalytic degradation of organic dyes and inhibit bacterial growth

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ABSTRACT

Bio-inspired eco-friendly gold nanoparticles were synthesized by a green method using aqueous *Plumeria alba* flower extract (PAFE). The use of 1% and 5% concentrations of PAFE resulted in two different sizes of *P. alba* gold nanoparticles, PAGNPs1 and PAGNPs2, with surface plasmon resonance (SPR) peaks at 552 and 536 nm, respectively. Size-controlled formation of gold nanoparticles was indicated by the SPR shift observed with increasing concentration of PAFE. The accurate size and morphology of PAGNPs1 and PAGNPs2 were determined by transmission electron microscope (TEM) analysis is found to be 28 ± 5.6 and 15.6 ± 3.4 nm, respectively, and those are spherical in shape. The antibacterial activity of PAGNPs1 and PAGNPs2 was tested against *Escherichia coli*; the small-sized PAGNPs2 exhibited better antibacterial activity with a 16-mm zone of inhibition at a concentration of 400 μg/mL. Furthermore, the catalytic activity of PAGNPs1 and PAGNPs2 was analyzed on six hazardous dyes; PAGNPs2 exhibited more pronounced catalytic activity than PAGNPs1. Among all of the dyes, 4-nitrophenol was most rapidly degraded to 4-aminophenol by PAGNPs2 within 5 min. The mechanism of catalysis in the presence of PAGNPs1 and PAGNPs2 can be described as an electron transfer process from donor $NaBH_4$ to an acceptor. The facile green synthesis of such eco-friendly nanoparticles in bulk suggests this method has potential industrial applications.

Introduction

In the past few decades, small-sized metal nanoparticles have found extensive application in diverse fields including biomedical (Jain, Huang, El-Sayed, & El-Sayed, 2008), pharmaceutical (Chen et al., 2003), cosmetics (Ghodake & Lee, 2011), catalysis (Pradhan, Pal, & Pal, 2001), and water treatment (Li et al., 2008). Chemical methods used for the synthesis of metal nanoparticles involve the use of reducing agents such as sodium borohydride, *N*,*N*-dimethyl formamide, and trisodium citrate (Nor Kamarudin & Mohamad, 2010), whose processing byproducts are hazardous to the environment. To avoid the use of toxic chemicals in synthesizing metal nanoparticles, green strategies using biological entities have received significant attention in recent years because they are ecofriendly and involve a simple methodology (Raveendran, Fu, & Wallen, 2003). Among the green methods, plant mediated synthesis of metal nanoparticles is advantageous over microbial methods owing to its cost effectiveness, rapid synthesis, improved stability, and a wide range of biological activities owing to the presence of various phyto-compounds.

The green method of synthesizing metal nanoparticles involves noble metals such as Pt, Au, Ag, Cu, and Zn, among whom Au exhibits a unique and tunable surface plasmon resonance (SPR) (Khalil, Ismail, & El-Magdoub, 2012). Gold nanoparticles (GNPs) possess various colors based upon their size, shape, and aggregation ability. Previous reports on the synthesis of gold nanoparticles include the use of plants such as *Cassia auriculata* (Kumar et al., 2011), *Medicago sativa* (Gardea-Torresdey et al., 2000), *Aloe vera* (Chandran, Chaudhary, Pasricha, Ahmad, & Sastry, 2006), *Pelargonium graveolens* (Shankar, Pasricha, & Sastry, 2003), *Tamarindus indica* (Ankamwar, Chaudhary, & Sastry, 2005), and *Coriandrum sativum* (Narayanan & Sakthivel, 2008). Because the GNPs possess a high surface area and various sizes as well as shapes, they are also widely used in catalysis.

Dyes are major environmental pollutants extensively used in textiles, cosmetics, food, leather, and plastic industries and disposed into water bodies. These dyes generate toxic effects upon aquatic life and can be mutagenic or carcinogenic in nature, and

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the nitro and azo compounds present in these dyes take lengthy times to degrade and can accumulate in deep soils and remain indefinitely. Many processes have been developed to treat these dyes based upon photoelectric degradation (Lin, Zong, Zhou, & Zhu, 2009), adsorption (Safarik, Ptackova, & Safarikova, 2002), microwave-assisted degradation (Oturan, Peiroten, Chartrin, & Acher, 2000), and photo catalytic reduction (Bo, Zhang, Quan, & Zhao, 2008). However, all of these processes involve the use of organic solvents and are energy consuming. In these circumstances, modern methods based upon bio-green nanoparticles to treat these hazardous dyes are an attractive alternative approach because they are uncomplicated and can be operated under mild conditions.

This study reports a simple and green method for synthesizing gold nanoparticles using an aqueous extract of *Plumeria alba* flowers (PAFE). The PAFE contains a mixture of phyto-compounds including amyrinacetate, amyrins, ß-sitosterol, scopotetin, the iridoid isoplumericin, plumieride, plumieride coumerate, and plumieride coumerate glucoside (Gilman & Watson, 1994). The synthesized *P. alba* gold nanoparticles (PAGNPs) are characterized by ultraviolet–visible (UV–visible) spectroscopy, dynamic light scattering (DLS) particle size analysis, transmission electron microscopy (TEM)–energy dispersive X-ray spectroscopy (EDAX), fourier transform infrared spectroscopy (FTIR), thermo gravimetric–differential scanning calorimetry (TG–DSC), and X-ray diffraction (XRD) analysis. The antibacterial potential of the PAGNPs is analyzed against *Escherichia coli*. The catalytic property of PAGNPs to degrade different organic dyes such as methylene blue (MB), eosin Y (EY), 4-nitrophenol (4-NP), methyl red (MR), Congo red (CR), and ethidium bromide (EB) is analyzed.

Materials and methods

Materials

Plumeria alba flowers were collected from the Pondicherry University campus, washed with deionized water, shade dried and powdered. The $HAuCl_4$ (99.9%) was obtained from Sigma-Aldrich (Bangalore, India), and all of the other chemicals were also purchased from Sigma-Aldrich (Bangalore, India) and from Hi-Media (India). Reagents were purely analytical grade and used without any further purification.

Preparation of flower extract

Typically, the amount of 1 and 5 g of flower powder was separately mixed with 100 mL of deionized water in 250 mL Erlenmeyer flasks and kept in an orbital shaker overnight at room temperature. The supernatant was repeatedly filtered through Whatman No. 1 filter paper and the resulting extract was stored at 4 °C for further use.

Green synthesis of gold nanoparticles

About 10 mL of 1% and 5% PAFE was added separately to 25 mL of $HAuCl_4$ (1 mM) aqueous solution at room temperature, whereupon two minutes of incubation produced a noticeable color change in the reaction mixture from yellow to pink or blue, depending upon the concentration of flower extract. The color change of the reaction mixture is the indication of the formation of PAGNPs, which was further confirmed by UV–visible spectroscopy. The synthesized nanoparticles were collected by centrifugation (18,000 rpm), washed with distilled water, air dried and used for further analysis.

Characterization of gold nanoparticles

Bio-reduction and the formation of PAGNPs was periodically monitored using a UV–visible spectrophotometer (UV-1700, Shimadzu, Japan) at wavelengths between 350 and 700 nm, where the UV–visible spectrum of the PAGNPs at different time intervals was recorded. The average size and size distribution of the samples labeled PAGNPs1 (synthesized with 1% PAFE) and PAGNPs2 (synthesized with 5% PAFE) in liquid colloidal solution was measured by DLS instrumentation (Zetasizer Nano ZS, Malvern Instruments, UK).

Morphology and the elemental composition of PAGNPs1 and PAGNPs2 samples were examined using TEM (Tecnai G2 30, FEI, USA) and an EDAX analyzer (SEM S-4500, Hitachi, Japan). Samples were prepared by dropping the nanoparticle colloidal solution in methanol onto an aluminum-coated copper grid and placed at a 20 kV potential.

Functional groups present in the PAFE involved in the formation of the PAGNPs were analyzed by FTIR (Thermo Nicolet Nexus 6700 spectrometer, Thermal Electron Corporation, USA) analysis. The nano-powder and PAFE samples were uniformly mixed with potassium bromide (KBr) and compressed with a hydraulic press to prepare disks, which were then used for FTIR analysis. The measurements were carried out between 500 and 4000 cm^{-1}.

The thermal behavior and weight loss of the PAGNPs were studied by TG-DSC (SDT Q600 and Q20 DSC, TA Instruments, USA).

The crystalline nature of the synthesized PAGNPs was studied by XRD (Bruker D8 series) analysis. The sample was prepared using a thin powder of PAGNPs on a clean glass slide and the analysis was carried out using monochromatic Cu $K\alpha$ radiation running at 40 kV and 30 mA with a step size of 0.005°.

Antibacterial activity

The antibacterial activity of the green-synthesized PAGNPs1 and PAGNPs2 samples was evaluated using *E. coli* via the modified disc diffusion method of Kirby–Bauer (Pal, TaK, & Song, 2007). The antibacterial potential was screened using mueller hinton agar (MHA), where the MHA plates were prepared by pouring 20 mL of molten media into sterile Petri plates. The plates were allowed to solidify for 5 min, whereupon 100 μL of inoculum suspension was swabbed uniformly on the surface and allowed to dry for 5 min. Different concentrations (200, 300, and 400 μg/mL) of the PAGNPs1 and PAGNPs2 samples were loaded on 3 mm-diameter sterile individual discs, which were placed on the surface of the medium and the compound was allowed to diffuse for 5 min, after which the plates were kept for incubation at 37 °C for 24 h.

The growth inhibitory effect of the PAGNPs1 and PAGNPs2 samples in *E. coli* was studied using three different PAGNP concentrations like 200, 300, and 400 μg/mL. Under normal growth conditions, bacterial growth is comprised of four different phases, including the lag, log, stationary, and decline phases. In this study, the growth pattern of the *E. coli* culture with and without PAGNPs1 and PAGNPs2 was measured at regular time intervals using the UV–visible spectrophotometer at 600 nm wavelengths, and the growth curves are plotted.

Catalytic experiments

The catalytic activity of PAGNPs1 and PAGNPs2 was analyzed on various dyes. First, 1 mL of freshly-prepared sodium borohydride ($NaBH_4$) (0.150 M) solution was separately added to 1 mL of MB (10 mM), 1 mL of EY (10 mM), 0.3 mL of 4-NP (10^{-5} M), 1 mL of MR (10 mM), 1 mL of CR (1 mM), and 1 mL of EB (1 mM). The volume of the reaction mixture was totaled to 3 mL, whereupon 0.2 mL of PAGNPs1 and PAGNPs2 (50 μg/mL) were added individually to