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Photocatalytic reduction of organic pollutant under visible light by green route synthesized gold nanoparticles

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ABSTRACT

We report a rapid method of green chemistry approach for synthesis of gold nanoparticles (AuNPs) using *Lagerstroemia speciosa* leaf extract (LSE). *L. speciosa* plant extract is known for its effective treatment of diabetes and kidney related problems. The green synthesis of AuNPs was complete within 30 min at 25°C. The same could also be achieved within 2 min at a higher reaction temperature (80°C). Both UV–visible spectroscopy and transmission electron microscopy results suggest that the morphology and size distribution of AuNPs are dependent on the pH of gold solution, gold concentration, volume of LSE, and reaction time and temperature. Comparison between Fourier transform infrared spectroscopy (FT-IR) spectra of LSE and the synthesized AuNPs indicate an active role of polyphenolic functional groups (from gallotannins, lagerstroemin, and corosolic acid) in the green synthesis and capping of AuNPs. The green route synthesized AuNPs show strong photocatalytic activity in the reduction of dyes viz., methylene blue, methyl orange, bromophenol blue and bromocresol green, and 4-nitrophenol under visible light in the presence of $NaBH_4$. The non-toxic and cost effective LSE mediated AuNPs synthesis proposed in this study is extremely rapid compared to the other reported methods that require hours to days for complete synthesis of AuNPs using various plant extracts. Strong and stable photocatalytic behavior makes AuNPs attractive in environmental applications, particularly in the reduction of organic pollutants in wastewater.

Introduction

Gold, a precious metal, is mainly used for ornamental and trading purposes. Nano-sized gold particles (AuNPs; ≤100 nm) are used in a variety of applications (*e.g.*, biomedical, catalysis, and electronics) as its unique chemical, optical, and electromagnetic properties largely depend on the size and shape of nanoparticles (Daniel and Astruc, 2004). AuNPs are commonly synthesized by either top-down (larger to nano-sized) or bottom-up (atomic to nano-sized) approaches, which also generate toxic byproducts (Thakkar et al., 2010). Therefore, to avoid hazardous waste generation associated with conventional

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AuNPs synthesis, an environmentally safe, green chemistry approach is desired that makes use of only biomaterials for AuNP synthesis. In this regard, a large number of biological methods have been reported for AuNPs synthesis using widely available natural biomaterials, mainly micro-organisms or plants (Thakkar et al., 2010). The plant extract mediated bio-synthesis is popular due to the wide availability of plants as well as the economical and non-toxic nature of synthesis (Gan et al., 2012). Several plant extracts have been reported as potential bio-reducing agents for AuNPs synthesis, *e.g.*, *Syzygium aromaticum* (Raghunandan et al., 2009), *Cassia auriculata* (Kumar et al., 2011), *Sesbania grandiflora* (Das and Velusamy, 2014), *Ficus racemosa* (Tetgure et al., 2015).

AuNPs have recently been recognized as a new class of catalyst due to its high optical absorption properties under both ultraviolet (UV) and visible light irradiation (Thompson, 2007; Zhu et al., 2009). The catalytic activity of AuNPs is due to its negative redox potential, which is smaller than that of the bulk metallic gold (Laoufi et al., 2011). The use of AuNPs as catalysts in photocatalytic degradation/reduction of pollutant has become popular (Gupta et al., 2010; Lu et al., 2011; Gangula et al., 2011; Cheng et al., 2013; Narayanan and Park, 2015). Because widely used photocatalyst like TiO_2 nanoparticles required UV light for its catalytic activity, which is the major drawback due to the limited amount of UV in solar light (Sarina et al., 2013). Unlike TiO_2, AuNPs, which absorb visible light, act as an electron relay system between the organic pollutant and the reducing agent and facilitate the degradation/reduction of pollutant (Ahmad et al., 2015).

This study reports rapid bio-synthesis of AuNPs using plant aqueous extract prepared from *Lagerstroemia speciosa* (Lythraceae), also called Banaba, a tropical plant commonly found in Southeast Asia. *L. speciosa* has antidiabetic activity and it contains bio-active components, such as tannins and corosolic acid (Murakami et al., 1993; Miura et al., 2004; Liu et al., 2005). Although, *L. speciosa* leaf extract has been used for the synthesis of AgNPs (Sundararajan and Kumari, 2014), to the best of our knowledge this has not been used for AuNPs bio-synthesis (Noruzi, 2015). We have studied the effects of various reaction parameters, including the pH of gold solution, gold ions concentration, the volume of *L. speciosa* leaf extract (4%), and the reaction time and temperature on the extent of bio-synthesis of AuNPs. The microstructure and phase of the bio-synthesized AuNPs were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Fourier transform infrared spectroscopy (FT-IR) was carried out to determine the role of active functional groups in the nanoparticle synthesis. Further, we have investigated the photocatalytic activity and catalytic stability of the bio-synthesized AuNPs in reduction of dyes and a nitro aromatic compound by $NaBH_4$ under visible light.

1. Materials and methods

1.1. Preparation of *L. speciosa* leaf extract

L. speciosa plant leaves were collected from the Indian Institute of Remote Sensing campus, Dehradun, India. Leaves were washed with tap water followed by ultrapure water (18.2 mΩ/cm at 25°C) to remove dust particles and were then air-dried at room temperature for two days. The dried leaves were powdered using a simple blender and the fraction ≤250 μm was collected after passing the leaf powder through an ASTM 60 mesh sieve. About 4 g of powdered leaves were added to 100 mL of sterile ultrapure water in a 250 mL Erlenmeyer flask. The mixture was heated in a water bath at 60°C for 10 min. Subsequently, the solution was vacuum-filtered through Whatman filter paper (No. 40, 8 μm) to collect the *L. speciosa* leaf extract (LSE). The LSE was refrigerated at 4°C prior to use for bio-synthesis of AuNPs. An appropriate concentration of gold solution was prepared by dissolving 99.99% pure chloroauric acid ($HAuCl_4$, Sigma-Aldrich, USA) in 2% HCl solution. All other chemicals used were of AR grade from Merck.

1.2. Bio-synthesis of AuNPs along with a control experiment

A controlled experiment was carried out for bio-synthesis of AuNPs in which 100 μL of (4%) LSE solution was added to 10 mL of 50 ppm aqueous solution of gold ions in a 50 mL vial, thoroughly shaken by hand, and left for 30 min at 25°C. The color of the solution changed rapidly from light pale yellow (of gold ions) to ruby pink in 30 min suggesting the formation of AuNPs. Parallel sets of experiments were initiated to study the effect of various parameters, such as the pH of the gold solution (1.0–6.0), the concentration of gold ions (10–150 ppm), the volume of LSE solution (50–500 μL), the reaction time (0–50 min), and reaction temperature (25–100°C). These results were compared with the control experiment to assess the role of controlling parameters on the bio-synthesis of AuNPs.

1.3. Characterization of the bio-synthesized AuNPs

In this study, a double beam UV–visible spectrometer (Lamda-25, Perkin-Elmer, USA) working in the wavelength ranges of 200–1100 nm with a resolution of 1 nm was used to get the absorption spectra of the solution containing bio-synthesized AuNPs. All analyses were carried out in 10 mm quartz cuvettes. The morphology (size and shape) of the bio-synthesized AuNPs was studied using transmission electron microscopy (TEM) at the Indian Institute of Technology Kanpur (IITK). For this morphology study, a sonicated (for 30 min) suspension of AuNPs was loaded on a carbon–coated copper grid of 200 mesh size and dried in an oven at 90°C prior to analysis. All images were taken in bright field using TEM (Tecnai G2, FEI, USA) operated at 200 kV. The particle size distribution of AuNPs was determined by a particle size analyzer (NanoBrook 90Plus Brookhaven Instruments Corporation, USA) using the dynamic light scattering technique in which the measurements are recorded at a 90° angle with respect to the incident beam. The crystallinity of LSE mediated bio-synthesized AuNPs was confirmed by X-ray diffraction (XRD). A few drops of the synthesized solution was added onto a glass plate and dried at 60°C overnight. Analyses were carried out using the XRD (X'Pert^3 Powder, PANalytical, USA) at IITK, operated at 45 kV and 35 mA, Cu Kα radiation, and 2θ scan in the range 10–100°.

Fourier transform infrared spectroscopy (FT-IR) analyses were performed to identify the functional group(s) of biomolecules present in the LSE solution that was responsible for

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