Ecofriendly ultrasound-assisted rapid synthesis of gold nanoparticles using *Calothrix* algae

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Abstract

In the present work we demonstrate the ultrasound assisted synthesis of gold nanoparticles (AuNPs) in an ecofriendly manner using *Calothrix* algae. The production of the AuNPs in the reaction mixture is significantly accelerated by inducing ultrasound irradiation. The optical property, size distribution, morphology and crystalline phase of the AuNPs were determined by visual, UV–vis spectroscopy, dynamic light scattering, transmission electron microscopy (TEM) and x-ray diffraction (XRD) technique. The appearance of a light pink color at $\lambda_{\text{max}} = 550 \, \text{nm}$ indicated the synthesis of AuNPs. TEM images showed the formation of anisotropic AuNPs with predominant truncated shape and particles are in the range of 30–120 nm. The XRD spectrum of the AuNPs exhibited a Bragg reflections peak at 38.23°, corresponding to elemental gold. 

Further, AuNPs showed significant catalytic efficiency (rate constant, $k = 0.072 \, \text{4752 min}^{-1}$) in reducing 4-nitrophenol (2 mM) to 4-aminophenol. The advantage of using ultrasound relates to the ecofriendly and rapid synthesis of AuNPs and various biotechnological applications were suggested.

Keywords: *calothrix*, gold nanoparticles, ultrasound assisted synthesis, catalysis

Classification numbers: 2.04, 4.02, 5.00, 5.06

1. Introduction

An important aspect of nanobiotechnology is to design economical and ecofriendly technique for the synthesis of nanomaterials and advancing the use of nanotechnology based materials in different applications. Although several chemical and physical methods are reported for the preparation of various metal nanoparticles, but they produce numerous non-biodegradable and hazardous byproducts, which are harmful to the environment [1]. However, for a biological process to successfully compete with chemical and physical nanostructure synthesis, strict control over average particle size in a specific size range and uniform particle morphology is required [2]. Gold is a noble metal and its nanoparticles are highly demanded for different applications in various fields due to its low toxicity. Biosynthesis of gold nanoparticles (AuNPs) using bacteria [3], fungi [4], enzymes [5], biomolecules [6] and plant materials, including flower [7], fruit [1], leaf [8], seed [9], oil [10] etc, have become an attractive ecofriendly alternative option as compared to the chemical and physical methods.

Algae/alga is the naturally available plant and consider as an important source of carbohydrates, protein and lipids. Interestingly, there are few works reported in the literature for the synthesis of AuNPs using algae/alga including *Fucus vesiculosus* [11], *Tetraselmis kochiensis* [12], *Prasiola crispa* [13], *Padina gymnospora* [14], *Sargassum muticum* [15], *Turbinaria conoides* [16], *Chlorella vulgaris* [17], etc.
It is already reported from several studies that the use of ultrasound irradiation can accelerate a wide range of chemical reactions and extraction procedures. Besides, the cavitation collapse produces intense local heating and high pressures in the liquid reaction mixture, with very short lifetimes. These transient, localized hot spots have an equivalent temperature (~1000°C) and a pressure (~2000 atmospheres, that can cause the reaction to take place rapidly [18].

To the best of our knowledge, there are few publications concerning the combination of phytochemical and an ultrasound assisted method for the synthesis of nanoparticles. In this regards, ultrasound assisted synthesis of AuNPs using Calothrix algae is more economical and ecofriendly than other physio-chemical procedures. The optical property, size distribution, morphology and crystalline phase of the AuNPs were determined by different analytical instruments. Further, as-synthesized AuNPs were investigated as catalyst for the synthesis of 4-aminophenol (4-AP) from 4-nitrophenol (4-NP) via one step reduction process.

In general, 4-AP is an important chemical intermediate for the preparation of pharmaceuticals, dyes, pesticides, photographic developers, etc. It is synthesized by multi-step iron-acid reduction of 4-NP or 4-nitro chlorobenzene. So, a single-step catalytic hydrogenation of 4-NP to 4-AP using nanoparticles is gaining more importance because of simple technology, high product yield and ecofriendliness [19].

2. Experimental

2.1. Ecofriendly ultrasound-assisted synthesis of AuNPs

Gold chloride (AuCl₄⁻, 99.0%) and 4-nitrophenol (>99.5%, 4-NP) were purchased from Spectrum, USA. Sodium borohydride (NaBH₄, >99.5%) was purchased from Sigma Aldrich, USA. Calothrix algae was kindly provided by Dr Ever Morales Avendaño, Universidad de las Fuerzas Armadas ESPE, Sangolqui, Ecuador. For ecofriendly synthesis of AuNPs, 3 mg of Calothrix algae was added to 10 ml of 0.1 mm AuCl₄ solution and the reaction mixture were incubated for 3 d at 22°C–25°C. Then, 3 d incubated AuNPs was ultrasonicated for 10 min and color of the mixture solution had become a light pink color due to the formation of the AuNPs. Ultrasound assisted synthesis was performed with ultrasonic processors (DAIGGGER GE 505, 500 W, 20 kHz) immersed directly into the reaction solution. The operating condition was at 30 s pulse on/30 s pulse off time with amplitude of 72% at 25°C for (5 x 2) min. The synthesized AuNPs were characterized further using different analytical instruments.

2.2. Catalytic activity of AuNPs for the reduction of 4-NP to 4-AP

To test the catalytic efficiency of AuNPs, reduction of 4-NP was carried out as a model reaction and monitored as follows: about 0.2 ml of 4-NP (2 mm), 0.2 ml of as synthesized AuNPs and 3.4 ml of H₂O were mixed in a 4 ml standard quartz cuvette. To this reaction mixture, 0.2 ml of NaBH₄ (0.05 mm) solution was added and UV–vis absorption spectra were recorded at 1 min intervals, leading to a color change from pale yellow to colorless. Control reactions were also monitored for 15 min in the absence of AuNPs or NaBH₄ keeping other parameters constant. The observed rate constant (k) of the reduction process was determined by analyzing the change in an intensity of the peaks at 400 nm as a function of time. The concentration of 4-NP at time t is denoted as Cₜ, and the initial concentration of 4-NP at t = 0 is regarded as C₀. The kC₀/Cₜ is measured from the relative intensity of absorbance (A₀/Aₜ). The linear relationship of ln(A₀/Aₜ) versus time indicates that the reduction of 4-NP by AuNPs follows the first order kinetics [20].

2.3. Characterization of AuNPs

The UV–vis spectrum was measured using a Thermo Spectronic, GENESYS™8, England spectrophotometer. The particle size distributions of nanoparticles were determined using the dynamic light scattering, DLS (HORIBA, Version LB-550 program). Size and selective area electron diffraction (SAED) pattern of nanoparticles are studied on transmission electron microscopy, TEM (FEI, TECNIAL, G2 spirit twin). X-ray diffraction (XRD) studies on thin films of the nanoparticle were carried out using a PANalytical brand ~θ–2θ configuration (generator-detector) x-ray tube copper λ = 1.54 Å and EMPYREAN diffractometer.
room temperature and ultrasound technique. In figures 1(a) and (b), it clearly indicated that the synthesis of AuNPs is enhanced under the assistance of ultrasound and the color of AuNPs rapidly changes to light pink. This observation was confirmed by the UV–vis spectrum (figures 1(c) and (d)) and the appearance of the surface plasmon resonance (SPR) peak of the colloidal AuNPs at $\lambda_{\text{max}} = 550$ nm [21]. However, there is no SPR peak observed for the AuNPs incubated for 3 d at room temperature.

3.2. DLS study

Figure 2 depicted the DLS size distribution histogram for AuNPs synthesized at room temperature for 3 d and ultrasound treatment using Calothrix algae. The average particle size of the AuNPs synthesized before and after ultrasound treatment was found to be 3789.1 ± 1173 nm and 238.9 ± 275.4 nm, respectively. It was observed that, the size of as-synthesized AuNPs at room temperature was bigger than ultrasound assisted method. It may be either due to the intact of AuNPs inside the algal cells or less synthesis of AuNPs. But after ultrasound treatment, the synthesis of AuNPs was enhanced and observed size was small, ranging from 40 to 300 nm.

3.3. TEM study

The morphology, size and crystallinity of the as-synthesized AuNPs were investigated by TEM and SAED measurements. Figures 3(a) and (b) show that the AuNPs synthesized using the Calothrix algae under the influence of ultrasound irradiation are anisotropic in nature and size ranging from 30 to 120 nm. In addition to truncated and spherical shape AuNPs, some triangular shape AuNPs (figure 4(a)) also observed. The partial concentric rings of the SAED spots clearly verifies the existence of polycrystalline nature of AuNPs (figure 3(c)). However, the square lattice pattern (figure 4(b)) of the triangular AuNPs represents the monocrystalline nature and crystal growth towards the (111) plane [22]. The observed size of AuNPs in TEM analysis is smaller than DLS analysis, it may be either due to the involvement of algal phytochemicals on the surface of AuNPs or screening of smaller AuNPs by a bigger one [23].

3.4. XRD study

As shown in figure 5, the Bragg reflection peak at 38.23° corresponds to the (111) lattice planes, which confirms the face centered cubic structure of the formed AuNPs (ICSD No. 98-005-3763). The broadening of Bragg’s peaks also indicates the formation of nanoparticles and the size of as-formed AuNPs was estimated by using Scherrer’s equation by determining the width of the (111) Bragg reflection. The observed size of AuNPs by XRD analysis was calculated to be around ∼57 nm and agreed with the result of TEM images corresponding to the truncated AuNPs.

3.5. Catalytic activity of AuNPs

Figure 6(a) shows the catalytic activity of AuNPs for the formation of 4-AP from 4-NP in the presence of NaBH4 and the reduction reaction is easily detected by UV–vis spectroscopic methods. It showed that the concentration of 4-NP in the form of 4-nitrophenolate ions at $\lambda_{\text{max}} = 400$ nm gradually
decreased with the concomitant appearance of a new peak at 298 nm due to the reduction of 4-NP to 4-AP \cite{24} and more than 63% of 4-NP reduction observed within 15 min at room temperature, respectively. In figure 6(b), the plots of $\ln(A_0/A_t)$ versus time yielded good linear correlations revealing that the NaBH$_4$ reduction of 4-NP catalyzed by AuNPs followed the first-order kinetics. The observed values of first-order rate constant ($k$) and correlation coefficients ($R^2$) were 0.072 4752 min$^{-1}$ and 0.9931, respectively. The cause behind the catalytic reduction of 4-NP by AuNPs may be either due to interfacial electron transfer or the rate of electron transfer at the AuNPs surface can be influenced by the diffusion of 4-NP to the metal surface, and the diffusion of 4-AP away from the surface \cite{25, 26}.

4. Conclusions

In conclusion, this study shows that the combination of Calothrix algae with ultrasound irradiation can be used efficiently for the rapid synthesis of truncated shape AuNPs having an average size in the range of 30–120 nm. The XRD spectrum confirms the presence of gold in AuNPs in the form of Au$^0$. In addition, the synthetic protocol is low cost, eco-friendly, and more active for the catalytic conversion of 4-NP to 4-AP under mild condition with rate constant, $k = 0.072 4752$ min$^{-1}$. Thus, the ecofriendly synthesized AuNPs has potential usefulness in remediation of toxic chemicals and other catalyst based industrial applications.
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