Biosynthesized Gold Nanoparticles as Catalyst

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Abstract— *Citrullus lanatus* (watermelon) fruit juice is a delicious multivitamin drink of great medicinal significances. Nutritionally, *Citrullus lanatus* is a good source of vitamin A and C. We have used this juice for the synthesis of gold nanoparticles (AuNP) under very gentle condition. The resulting AuNP has been used as a catalyst. The catalytic activity of the as-prepared gold nanoparticles was observed in the reduction reaction of 2, 4- Dinitrophenyl hydrazine to 2, 4-Diaminophenyl hydrazine in presence of $NaBH_4$. The reduction progression with time has been monitored from the UV-Vis spectra. No change in absorption spectrum was observed on addition of freshly prepared aqueous solution of sodium borohydride in 2, 4-DNP solution. Reduction of the nitro group to amino group only took place when AuNP solution was added in the mixture and the reaction was very fast. A new peak due to the reduction product (amino analogue) developed immediately at 300 nm as soon as AuNP solution was added and the peak due to the 2, 4-DNP at 358 nm was abolished. The intensity of the new peak gradually increased with time. Complete elimination of 358nm peak and subsequent emergence of 300 nm peak within a few minutes indicated the catalytic activity of the AuNP solution.

Index Terms Green synthesis, Gold nanoparticle, *Citrullus Lanatus*, UV-Visible spectroscopy, Catalytic reduction, 2, 4-dinitrophenyl hydrazine, 2 ,4-diaminophenyl hydrazine.

1 INTRODUCTION

Nanotechnology is an emerging field of science which involves synthesis and applications of nanoparticles. Metal nanoparticles are extensively used in various applications including electronics, bio sensing and surface enhanced Raman spectroscopy. During past two decades an enormous effort has been invested in the investigations of metal nanoparticles because of their applications including as vehicles for drug delivery, catalysts, biotechnology, biodiagonstics biosensors, imaging and visualizing agents etc [1-6]. Among the various applications catalysis at the nanoscale level has attracted significant attention in the past two decades due to the unique properties of materials that arise at that level [7]. Nanoparticles are important catalysts for pollutant removal [8], energy conversion [9, 10], etc. As compared to their bulk counterparts, nanoparticles are often superior or new catalytic properties result from their nanometer size, which gives them increased surface-to-volume and chemical potentials. The catalytic properties of AuNP have been explored. Gold nano catalysts have found a wide range of applications including CO oxidation [11], formic acid electro oxidation [12], alcohol dehydrogenation [13], etc. Tsunoyama et al. have used colloidal AuNP as catalyst for carbon-carbon bond formation [14]. Sau et al. have used gold nanoparticles for the reduction of Eosin [15].

AuNP can be synthesized by conventional chemical and physical methods [16-18]. Many of the synthetic routs for development of nanomaterials using of toxic reagents make them unsuitable for biological use and also have adverse effect on environment. So, development of green processes for the synthesis of nanoparticles has evolved into an important branch of nanotechnology. Green nanotechnology uses biomolecules present either in plant extracts or micro-organism as novel reducing and capping agents. They not only suffice as environmentally friendly routs but also economically sustainable alternatives to chemical and physical methods. Recently, many biosynthetic routs have been reported for the synthesis of AuNP through micro-organism such as algae, fungi and bacteria. However, due to their cumbersome procedure such as maintaining cell cultures under specified laboratory conditions have made them less attractive compared to plant products for synthesis of nanomaterials. So, the synthesis of AuNP by using renewable plant or plant products [19-25] has received tremendous attention in recent years.

In our present work, the synthesis of gold nanoparticles has been carried out using the juice extract of *Citrullus lanatus.* Nutritionally, the *Citrullus lanatus* is a good source of vitamin A and C. The thiamine, riboflavin, niacin, carbohydrates, lipids, proteins are the major polysaccharides present in it. Ascorbic acid is the most abundant organic acid with some pantothenic and folic acid [26]. Thus the *Citrullus lanatus* juice mostly contains proteins and water soluble organic acids. The presence of organic acids and polyphenols in the *Citrullus lanatus* juice may be responsible for the reduction of Au^{+3} to Au^0 ions and stabilization of AuNP.

2 MATERIALS AND METHODS

2.1 Chemicals

Chloroauric acid was of AR grade, purchased from Sigma-Aldrich Chemical Ltd. Sodium hydroxide and 2, 4-Dinitrophenylhydrazine (2, 4 DNP) and sodium borohydride were purchased from Merck. Double distilled de-ionized water was used in all experiments.

2.2 Preparation of juice extract

The *Citrullus lanatus* was collected from local market and washed with Double distilled de-ionized water. It was cut into pieces. The extract was made from the inner red portion of the fruit and it was filtered using whatman filter paper.

2.3 Synthesis of gold nanoparticles

AuNP was produced by reduction of Chloroauric acid solution using *Citrullus lanatus* juice extract. 5 ml of double distilled deionized water was added to 5 ml of pure juice extract to make it 1:1 and it was cooled in ice cold water. The solution was made alkaline (pH 10) by adding NaOH. The whole apparatus was placed on a heating mantle. During heating 6 ml 3×10^{-3}(M) aqueous chloroauric acid solution was added drop wise with continuous stirring from burette and finally it was heated further for 20 minutes at 70^0C. The color of the solution gradually changed from light pink to violet. The violet color indicated the formation of AuNP.

2.4 Characterization

The absorbance spectra of the AuNP were taken by using a 'SHIMADZU' UV 1800 spectrophotometer and for TEM images JEOL-JEM 2100 high resolution transmission electron microscope (HR-TEM) was used. Samples for the TEM studies were prepared by placing a drop of the aqueous suspension of particles on carbon-coated copper grids followed by solvent evaporation under vacuum.

2.5 Catalytic reduction of 2, 4 DNP induced by AuNP

The catalytic activity of the as-prepared AuNP was examined by the reduction of 2, 4-DNP to 2, 4-Diaminophenylhydrazine in presence of $NaBH_4$. 0.15 mM solution of 2, 4 DNP was prepared in ethyl alcohol and it was diluted 10 times with distilled water. The catalytic reduction was conducted using this diluted 2, 4 DNP solution at room temperature. For reduction, freshly prepared 200 µl of 0.125 mM $NaBH_4$ solution was added in 4ml of 2, 4 DNP solution. No change was observed visually as well as spectroscopically due to the addition of $NaBH_4$ only which confirms the failure of reduction. But, immediate occurrence of reduction was observed in presence of 250 µl of as prepared AuNP in the mixture.

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3 RESULTS AND DISCUSSIONS

3.1 UV-Visible spectral studies

In our present study, a smooth and narrow absorption band was observed at 540 nm due to the formation of gold nanoparticles using 1:1 composition of *Citrullus lanatus* juice extract (Fig. 1A). The *Citrullus lanatus* juice mostly contained proteins and water soluble organic acids like ascorbic acid, amino acids and vitamins. We believe that the organic acids as well as polyphenols have the major involvement in reduction as well as stabilization of AuNP.

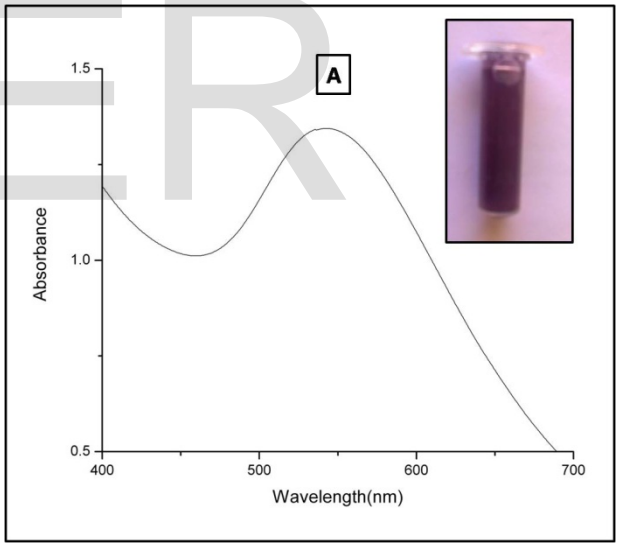

Fig 1: UV-Vis spectrum of (A) AuNP and (inset) the photographic image of AuNP prepared using *Citrullus lanatus*.

3.2 HR-TEM studies

The morphologies and the orientations of nanoparticles are generally observed from the TEM studies. Fig.2. shows the TEM image of AuNP produced from 1:1 composition of *Citrullus lanatus* extract. It is observed that the particles were mostly spherical and the hysteresis curve (Fig. 2C) for the particle size distribution confirmed that their sizes varied from 5 to 25 nm. Selected area diffraction pattern (SAED) illustrated the crystalline nature of the AuNP (Fig. 2B.)

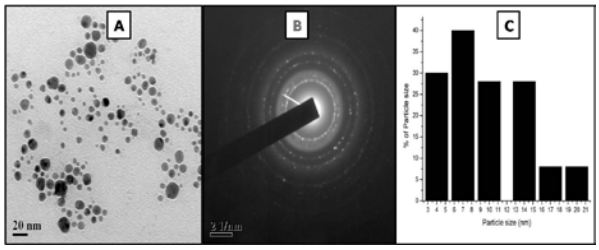

Fig. 2(A) is the TEM micrograph of AuNP. (B) Corresponding SAED pattern of AuNP. (C) The particle size distribution of AuNP.

3.3 FTIR spectral studies

FTIR analysis was performed to identify the biomolecules localized on the surface and responsible for the reduction of Chloroauric Acid. Representative FTIR spectra of pure *Citrullus lanatus* juice and the synthesized AuNP are shown in Fig. 3A and 3B respectively. The FTIR spectra before the bioreduction of Au^{+3} ions (Fig.3A) showed a broad spectrum between 3300-3600 cm^{-1} due to hydroxyl (OH) stretching bands of polyphenols and also might be due to the N-H group of pteridine ring of folic acid, riboflavins, thiamine, niacin etc [27]. The absorbance peak around 2934 cm^{-1} indicated the presence of aromatic C-H stretching [28]. The peak at 2858 cm^{-1}indicated the C-H stretching of aliphatic amines and the aromatic C-H out of plane deformation band occured below700 cm^{-1}. The absorbance peak at 1000-1200 cm^{-1} indicated C-O single bond and a peak at 1636 cm^{-1} indicated the presence of carbonyl group (C=O)form the polyphenols and organic acids such as folic acid, ascorbic acid. The absorbance peak at 1062 cm^{-1} corresponding to C-O stretching vibrations of alcohols, or phenols also confirmed the presence of polyphenols [29]. The broad spectrum at 3300-3600 cm^{-1} of pure *Citrullus lanatus* juice extract became slightly narrower and also slight change of band at 1636 cm^{-1} and disappearances of peak at1062cm^{-1} indicated the major involvement of polyphenols in the biosynthesis procedure.

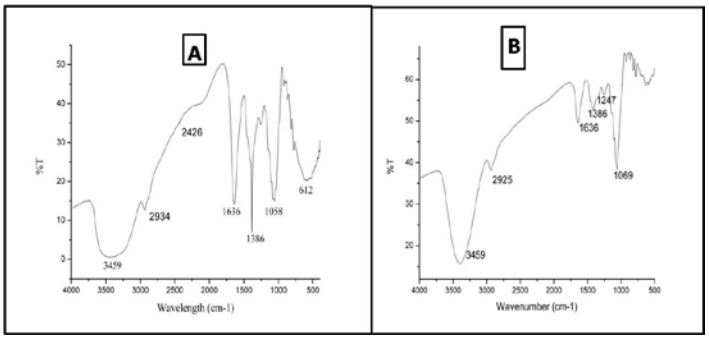

Fig. 3 FT-IR spectrum of vacuum-dried powder of (A) *Citrullus lanatus* juice and (B) AuNP synthesized from *Citrullus lanatus* juice.

3.4 Application of AuNP as catalyst

2, 4-DNP solution shows absorption maxima at 358 nm in UV-Visible spectrum. No change in absorption spectrum was observed on addition of freshly prepared aqueous solution of sodium borohydride in 2, 4-DNP solution. The picture did not change even keeping the solution for several days. Which suggests that the reduction of 2, 4-dinitrophenyl hydrazine by sodium borohydride is kinetically not favourable though the reduction reaction being thermodynamically favourable. Reduction of the nitro group to amino group only took place when AuNP solution was added and the reaction was very fast. A new peak due to the reduction product (amino analogue) developed immediately at 300 nm as soon as AuNP solution was added and the peak due to the 2, 4-DNP at 358 nm was abolished. The intensity of the new peak gradually increased with time. Complete elimination of 358nm peak and subsequent emergence of 300 nm peak within a few minutes indicated the catalytic activity of the AuNP solution.

To optimize the reaction condition and to establish the effects of AuNP and $NaBH_4$ on the reduction process, the experiment was carried out several times by changing the concentrations of both the precursors. The reaction was first carried out without adding NaBH4 in the solution mixture containing 2, 4 DNP and AuNP and stirred thoroughly. No peak due to the amino product generated but only two peaks were observed, one at 540 nm due to AuNP and another at 358 nm for 2, 4 DNP in the UV-Vis spectrum . So it confirms that AuNP itself is unable to reduce 2, 4 DNP. In an attempt to optimize the amount of $NaBH_4$ solution required to have reduction in presence of AuNP, amount of $NaBH_4$ was varied time to time. The experiment established that the minimum concentration of $NaBH_4$ required for reduction reaction to occur for 4 ml mixture of 2, 4- DNP and AuNP solution was 200 µl. The reduction tenure was observed for 10 minutes. During the reduction process the intensity of the peak due to the amino product increased appreciably. After 7 minutes of reaction time no further changes was observed. This indicated the completion of the reduction reaction. The relationship between ln (Ct/Co) and time (Fig. 4D) revealed a linear correlation, where Co and Ct are the concentrations of 2, 4- diamino phenyl hydrazine at time 0 and time t, respectively. The ratio of the absorbance, A_t/A_o here has been substituted for the ratio of the concentration, Ct/Co because the concentration of it is proportional to its absorbance.

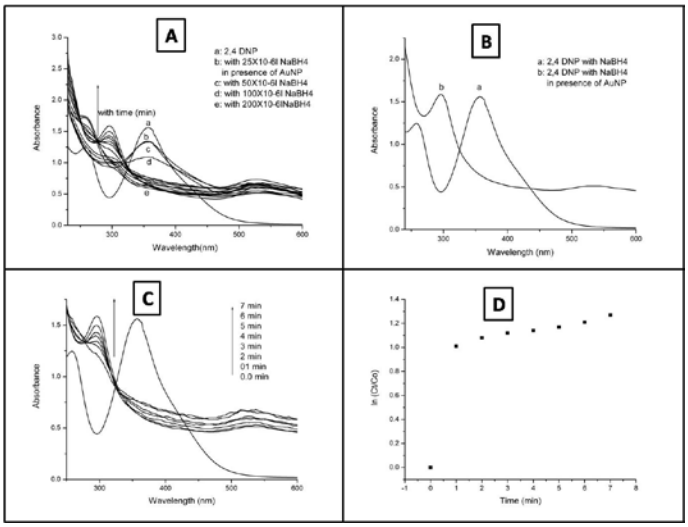

Fig. 4A: UV-Visible spectra of reduction reaction in presence of varied concentrations of $NaBH_4$; B: UV- Vis spectra of the mixture containing 2, 4-DNP and NaBH4 (a) in absence of AuNP and (b) in presence of AuNP. C: UV-Visible spectra of reduction reaction of 2, 4 DNP at varying time; D: plot of ln(Ct/Co) as a function of Time.

4 CONCLUSIONS

A very mild method for the synthesis of AuNP has been reported by using *Citrullus lanatus* juice, a well known multivitamin drink of great medicinal importance. The organic acids as well as polyphenols present in the juice extract were responsible for the reduction and stabilization of gold nanoparticles. The resulting AuNP has been used as a catalyst. The catalytic activity of the as-prepared gold nanoparticles was observed in the reduction reaction of 2, 4- Dinitrophenyl hydrazine to 2, 4-Diaminophenyl hydrazine in presence of $NaBH_4$. No change in absorption spectrum was observed on addition of freshly prepared aqueous solution of sodium borohydride in 2, 4-DNP solution. Reduction of the nitro group to amino group only took place when AuNP solution was added and the reaction was very fast. A new peak due to the reduction product (amino analogue) developed immediately at 300 nm as soon as AuNP solution was added and the peak due to the 2, 4-DNP at 358 nm was abolished. The intensity of the new peak gradually increased with time. After 7 minutes of reaction time no further changes was observed. This indicated the completion of the reduction reaction.

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