Kinetic Study on Green Synthesis of Gold Nanoparticles Using *Bougainvillea Glabra* Leaf Extract

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Abstract

Development of eco-friendly process for the synthesis of nanoparticles is one of the main steps in the area of nanotechnology. Green synthesis of nanoparticles is the evolution of nanobiotechnology. It is a low cost, environment benign, nontoxic and large scale up process. In this study, Bougainvillea glabra leaf extract was used for the bioreduction of gold ions to nanoparticles. Reduction of $HAuCl_4$ *by polyphenols present in leaves of B.glabra at different temperature provides AuNPs* ($Au^{3+} \rightarrow Au^0$)*. Bioreduction process was carried out to study about the factors affecting the nanoparticles synthesis by changing the gold ion concentration and temperature. 1mM gold ion concentration and temperature125 ºC is more favorable for maximum production of gold nanoparticles. UV-vis spectrum was used to characterize these synthesized gold nanoparticles and the SPR band was observed at 565 nm. The gold nanoparticles are characterized by FTIR.This green synthesis method has many advantages over the chemical method because it reduces the use of toxic metals in the synthesis process and it is a single step eco-friendly method.*

Keywords: *Bougainvillea glabra*, Gold nanoparticle, concentration, temperature

Introduction

Green nanotechnology is an area with significant focus at present on the important objective of facilitating the manufacture of nanotechnology-based products that are eco-friendly and safer for all beings, with sustainable commercial viability. The “green synthesis” of metal nanoparticles receives great attention due to their unusual optical, chemical, photochemical, and electronic properties[1]. Metal nanoparticles, especially the noble metals, have mainly been studied because of their strong optical absorption in the visible region caused by the collective excitation of free-electron gas[2]. The biosynthesis of nanoparticles, which represents a connection between biotechnology and nanotechnology, has received increasing consideration due to the growing need to develop environmentally friendly technologies for material syntheses. The search for appropriate biomaterials for the biosynthesis of nanoparticles continues through many different synthetic methods[3]. In modern nanoscience and technology, the interaction between inorganic nanoparticle and biological structures are one of the most exciting areas of research. The biological synthesis process elucidates the importance of metal microbe interaction in several biotechnological applications including the field of bioremediation, biomineralization, bioleaching and microbial corrosion[4]. Nanomaterials are new, emerging and creating progress due to their interesting electrical, optical, magnetic and chemical properties than bulk materials. Noble metal nanomaterials are great attention in various fields due to their unique properties. Noble metals such as Ru, Pd, Ag, Pt and Au[5] are exhibiting a particularly wide range of material behavior along the atomic to bulk transition[6]. Gold nanoparticles have a great bactericidal effect on a several range of microorganisms; its bactericidal effect depends on the size and the shape of the particle[7]. In the present work *Bougainvillea glabra* leaves (Fig. 1) was used as a reductant for the synthesis of gold nanoparticles. Different conditions were employed for the synthesis of gold nanoparticles. To study the optimum factors for gold nanoparticles synthesis, the experiments were carried out at different gold ion concentrations and temperature conditions.

Figure 1 *Bougainvillea glabra* leaves

Materials and Methods

Materials for the preparation of Green gold nanoparticles

Chloro auric acid was purchased from Sigma Aldrich and de-ionized water was used for the preparation purpose. All the glass wares obtained from borosil and aqua regia was used for cleaning glassware as it can dissolve any residual metallic particles, which may interfere with the synthesis.

Collection of Plant material

Leaves were collected from Trichy District, Tamilnadu. The botanical identity of the plant of *B.glabra*was confirmed by the botany department of Holy cross college, Tiruchirappalli. The leaves were washed thoroughly 2–3 times with running tap water and the leaves are air dried under shade. After complete shade drying, the leaves were grinded in the mixer; the powder was kept in small plastic bags with proper labeling.

Preparation of extract

50 g of leaf powder was soaked in 250 ml of methanol. Then it was filtered and distillation was carried out to collect the crude and this process was repeated at regular intervals under cold percolation method. The extract was collected in amper bottle and refrigerated.

Phytochemical analysis

Phytochemical analysis involves the qualitative analysis of herbal plants. The preliminary qualitative tests have been attempted in *B.glabra* to find out the presence or absence of certain bio-active compounds. Chemical tests were carried out on the methanolic extract using standard procedures[8].

Synthesis of gold nanoparticles

1ml of 1mM chloro auric acid was mixed with 0.2 ml of *B. glabra* extract and kept in a room temperature for 20 hours. The color changes from yellow to ruby red color. This color change indicates the presence of green gold nanoparticles. The test was carried out using pilot experiments. The formation of GNPs was monitored by UV-visible and FTIR studies. Different conditions were employed for the synthesis of GNPs for optimizing the time of synthesis and color of GNP. Variation of concentration and temperature were two parameters which were varied for optimizing the process of synthesis of GNP[9].

Variation of concentration of chloroauric acid solution

The effect of variation of concentration of chloro auric acid with varying 1 ml of (1, 2, 3 and 4 mM of $HAuCl_4$ solution) was treated with 0.2 ml of the leaves extract. The formation of the GNPs was monitored by color identification and UV studies.

Variation of temperature

1 ml of chloro auric acid was treated with 0.2 ml of the leaves extract in different temperature such as 30 ºC, 100 ºC and 125 ºC. The effect of these parameters on the synthesis of gold nanoparticles was monitored by color and UV-Vis spectrophotometer.

Characterization of nanoparticles

UV-visible spectral analysis

The reduction of Au^{3+} to nanoparticle was monitored by measuring the UV-visible spectrum the most confirmatory tool for the detection of surface plasmon resonance property of AuNPs, by diluting a small aliquot of the sample in distilled water. UV-visible spectral analysis was done by using UV-Vis spectrophotometer systronics at the range of 300–600 nm.

Fourier transforminfra-red spectroscopy

Samples were measured by using spectral range of 4000–400 $cm^{-1}$with the resolution of the FTIR spectra of leaf extract taken before and after synthesis of Au NPs were analyzed the possible functional group for the formation of AuNps.

Results and Discussion

Phyto chemical screening of the methanolic extract of B.glabra

Standard phytochemical test were conducted to find out the presence of metabolites like alkaloid, flavonoids, terpenoids etc. The results of the phytochemicals were represented in the Table 1[10].

Table 1 Qualitative analysis of the phytochemicals of *B. glabra*

S. No.	Phyto chemicals	*B. glabra* leaves
1	Tannins	+
2	Phlobatannins	+
3	Saponin	+
4	Flavonoids	+
5	Steroids	+
6	Terpenoids	+
7	Cardiac glycosides	+

+ presence, – absence

Synthesis of gold nanoparticles using B. glabra

Visual observation

Formation of gold nanoparticles was preliminarily well known by changing of yellow to ruby red color while adding leaf extract with gold ion solution due to the excitation of free electrons in the nanoparticles[11]. The color formation was occurs within 20 hrs after addition of leaf extract at room temperature. Metal nanoparticles exhibits different colors in solution due to their optical properties. Gold nanoparticles were characterized by forming of ruby red color confirmed the completion of the reaction in Fig. 2 Previously, increasing color intensity with in 30 min was observed using leaf extract of *Acalyphaindica*[12].

Figure 2 Color change yellow to ruby red color indicate formation gold nanoparticles

UV spectral analysis

UV–Vis spectroscopy is an important technique to ascertain the formation and stability of metal nanoparticles. Figure 3 shows the UV–Vis spectra of the GNPs. Color of gold colloid is attributed to surface plasmon resonance (SPR) arising due to the collective oscillation of free conduction electrons induced by an interacting electromagnetic field[13]. SPR bands of the colloids are centered at 572 nm. The bands are broad and the intensity increases indicating increase in production of nanoparticles.

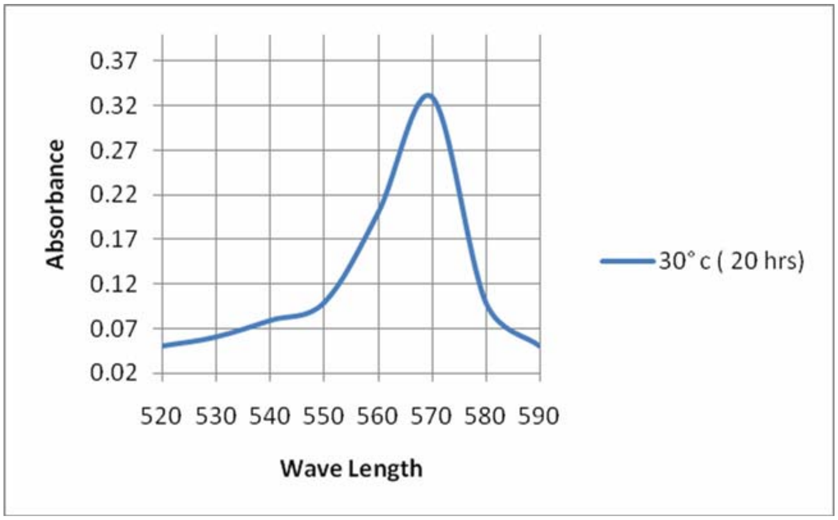


Fig. 3 UV spectrum of synthesis of gold nanoparticles

Effect of concentration variation of chloro auric acid

At the 1 mM concentration of chloro auric acid, narrow band with increased absorbance was found, whereas at 568 nm a broad peak was obtained. The absorption was increased while increasing the concentration of gold ions from 1mM to 4 mM. In 1 mM concentration the nanoparticles synthesis and size reduction was started quickly due to the more availability of functional groups in the leaf extract. The time taken for the formation of AuNPs in the variation of chloro auric acid is shown in the Table 2.

Table 2 Synthesis of GNPs by concentration variation method

Concentration of chloro auric acid (mM)	Concentration of leaves extract (ml)	Visual observation	SPR band (nm)
1	0.2	Ruby red color	568
2	0.2	Violet	574
3	0.2	Black	–
4	0.2	Black	–

The color changes from yellow to ruby red color , violet color and black color for 1mM to 4 mM of $HAuCl_4$ were noted in 20 minutes at 100 ºC (Fig. 4). The UV spectrum shows the SPR band in the regions of 568 nm and 574 nm (Fig. 5), This study shows that 1 ml of chloro auric acid is easily reduced by 0.2 ml of extract at 100 ºC in 20 minutes whereas the same reaction in room temperature took 20 hrs. While increasing the substrate concentration the large size and aggregation of nanoparticles was occurred due to the occurrence of compete between gold ions and functional groups of leaf extract. Thus, the optimization study showed a significant effect of concentration on the synthesis of gold nanoparticles. This investigation concludes that the optimum chloro auric concentration 1 mM is suitable for nanoparticles synthesis. Similarly, increasing intensity indicates increasing concentration of nanoparticles. Higher concentration of metal solution suggests the formation of larger nanoparticles[14].

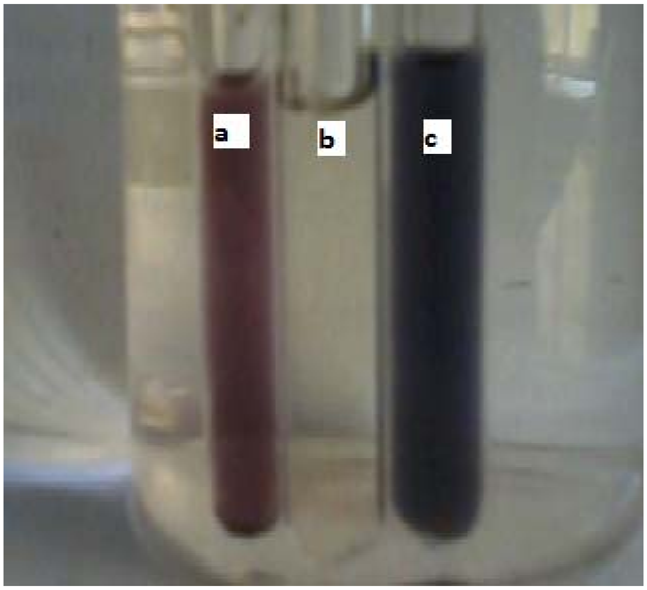


Figure 4 Effect of concentration variation of chloro auric acid.
(a)1mM GNPs, (b)1 mM $HAuCl_4$, (c)2 mM GNPs

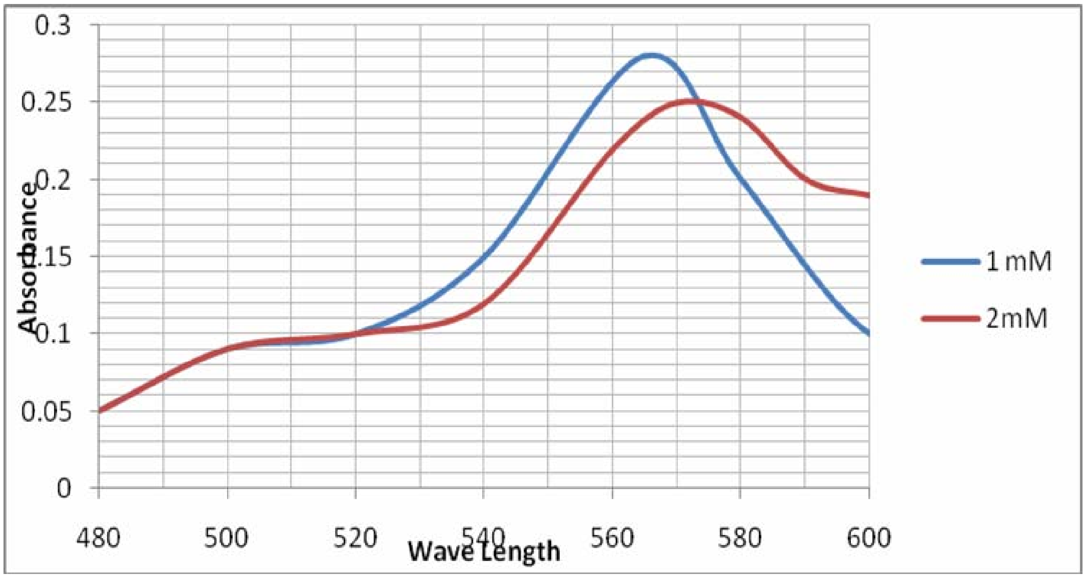


Figure 5 UV Spectrum of synthesis of gold nanoparticles at different concentration of $HAuCl_4$ Effect of temperature

Temperature is one of the important physical parameter on the synthesis of gold nanoparticles. Table-3 shows that the effect of temperature in the nanoparticles synthesis. The synthesis of nanoparticles was increases while increasing the reaction temperature by using the leaf extract of *B. glabra*. The absorbance band was broadened and positioned at 568 nm and 565 nm at the temperature of100 °C and 125°C, respectively (Fig. 6). The higher rate of reduction was occurred at higher temperature due to the consumption of gold ions in the formation of nuclei whereas the secondary reduction was stopped on the surface performed nuclei[15]. The broadening peak was obtained at low temperature shows formation of large sized nanoparticles and the narrow peak was obtained at high temperature, which indicates the formed nanoparticles are small in size and the higher rate of reduction of gold ions was occurred in the 125°C. Finally, it was concluded that higher temperature was optimum for nanoparticles synthesis[16].

Table 3 Synthesis of GNPs by temperature variation method

Temperature	Time duration	Visual observation	SPR band
30ºC	20 hrs	Ruby red color	572 nm
100ºC	20 min	Ruby red color	568 nm
125ºC	10 min	Ruby red color	565 nm

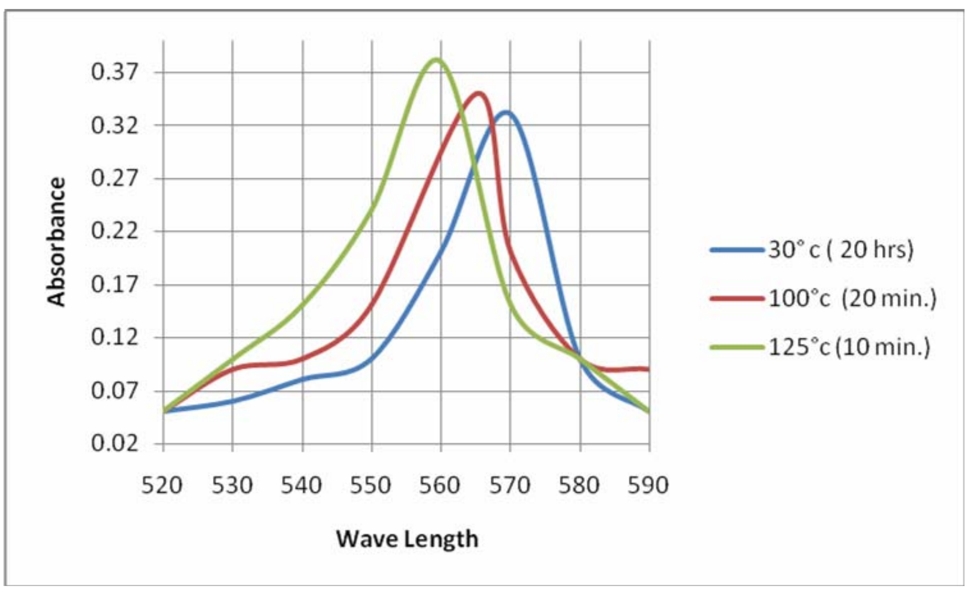


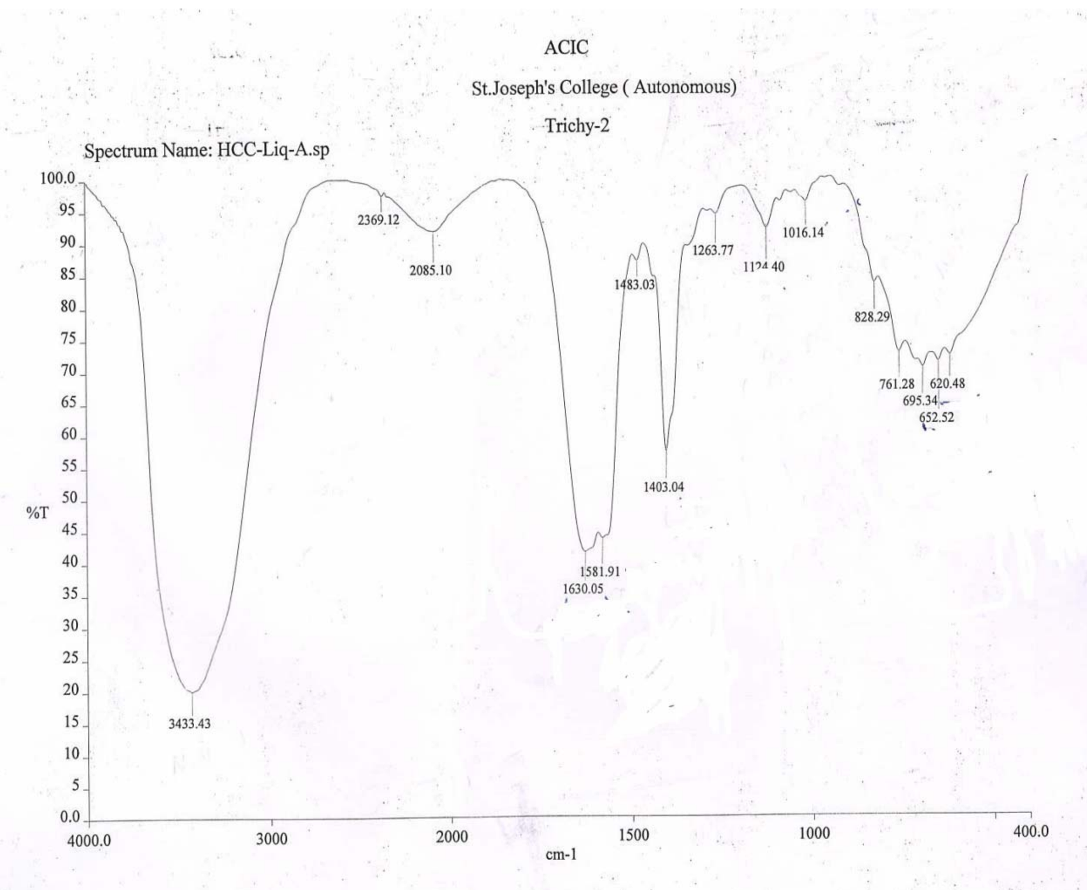
Figure 6 UV Spectrum of synthesis of gold nanoparticles at different temperatures

FTIR analysis

Functional groups identification

The FTIR spectrum was used to identify the functional groups of the active components present in extract based on the peaks values in the region of IR radiation. When the extract was passed into the FTIR, the functional groups of the components were separated based on its peaks ratio. The results of FTIR analysis confirmed the presence of alcohol, phenol, alkanes, aldehyde, aromatic compound, secondary alcohol, aromatic amines and halogen compound.

The IR spectra were recorded before and after the formation of green gold nanoparticle from the extract solution. The FTIR spectra of the extract showed bands at 3433 cm^{-1} assigned to O–H stretching vibration of alcohols and phenols, 1630 cm^{-1} assigned to C=O stretching vibration of tertiary amides,1263 & 828 cm^{-1} assigned to C–C–O stretching of epoxy rings and 1016cm^{-1} assigned to C=O stretching of primary alcoholand 652 cm^{-1} assigned to hydrogen bonded of -OH. The IR spectrum of gold nanoparticles showed a broad band contour which appear in the range of 3400-3467 cm^{-1}, it is due to the intermolecular hydrogen bond arise additional 3400-3467 cm^{-1} and 1634 cm^{-1} corresponds to C=O stretching vibration of tertiary amides. From these observations it is clear that the poly phenols present in the extract are responsible for the reduction and stabilization (Figure 7).



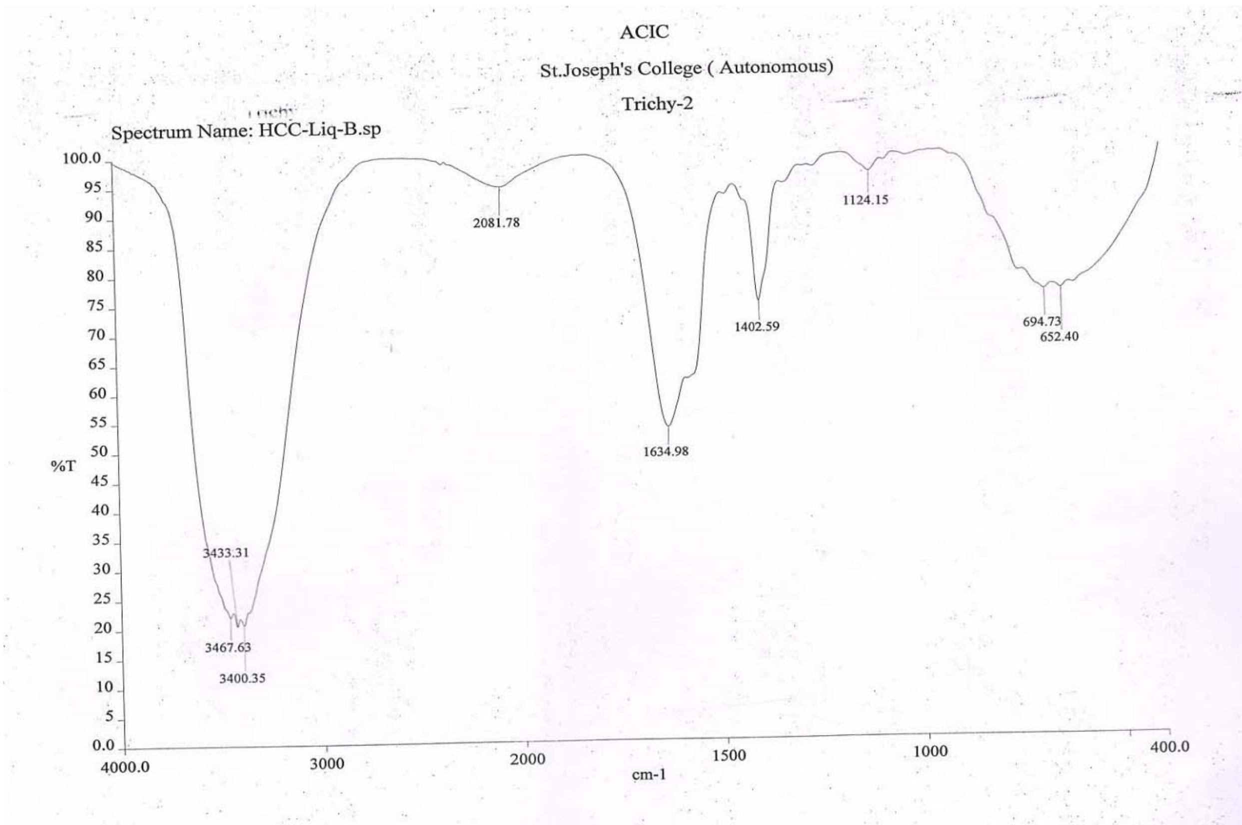


Figure 7 FTIR spectra of *B.glabra* leaf extract and gold nanoparticles

Conclusions

Biosynthetic route of nanoparticles synthesis will emerge as safer and best alternative to conventional methods. Green synthesis method of nanoparticles is evolution from the nano biotechnology. It is a low cost, environment benign, nontoxic and large scale up process.

i) In this study *B.glabra* leaf extract was used for the bioreduction of gold ions to nanoparticles. The *B. glabra* leaf extract contains flavonoids, terpenoids, tannins etc and also the antioxidant property.

ii) The antioxidant property and phyto compounds were used for the reduction of Au^{3+} to Au^0

iii) Bioreduction process was carried out to study about the factors affecting the nanoparticles synthesis by changing the gold ion concentration, and temperature.

iv) 1 mM gold ion concentration and temperature 125ºC is more favourable for maximum production of gold nanoparticles.

v) UV-Vis spectrum was used to characterize these synthesized gold nanoparticles and the SPR band was observed at 565 nm.

vi) The FTIR study shows the presence of alcohols in the sample may be responsible for the reduction and capping of Gold nanoparticles.

vii)This green synthesis method has many advantages over the chemical method because it reduces the use of toxic metals in the synthesis process and it was a single step eco-friendly method.

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