ORIGINAL PAPER

Green synthesis of gold nanoparticles using *Chrysophyllum cainito* (Star apple) leaf extract: An effective homogeneous catalyst for reduction reaction

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Abstract. The leaf extract of *Chrysophyllum cainito* has been exploited to synthesize stabilized colloidal gold nanoparticles (AuNPs) via an ecofriendly method. On addition of Au (III) salt to the aqueous leaf extract of *Chrysophyllum cainito*, the colorless solution turned reddish almost instantly which indicated the excellent efficacy of the leaf extract as reducing agent to reduce Au (III) to Au (0). The intensity of the red color was enhanced with time and this red color colloidal solution of AuNPs was stable for several months which confirmed the excellent efficacy of the leaf extract of *Chrysophyllum* caimito as stabilizing agent. The formation of stabilized AuNPs have been confirmed by UV-visible spectroscopy, high resolution transmission electron microscopy (HRTEM), dynamic light scattering (DLS) studies, and X-ray diffraction studies. The synthesized AuNPs have been utilized as efficient catalyst for reduction reaction of 3-nitrophenol and 4-nitrophenol with sodium borohydride.

Keywords: metal nanoparticles, green synthesis, Leaf extract of *Chrysophyllum cainito*, polyphenols, catalysis.

1. Introduction

Chrysophyllum cainito (C. cainito) is one of the species of Chrysophyllum Linn. (Sapotaceae) genus. In Thai, the plant is known as sata apoen, louk nom. This medicinally important plant, commonly known as Star Apple, is an evergreen ornamental plant which are available in the warmer parts of Asia. The leaves of this plant, widely used as antidiabetic medicine, contain different chemical compounds which include polyphenols and flavonoids (Das A et al. (2010), Koffi N et al. (2009), Shailajan S and Gurjar D (2014) and Meira NA et al. (2014)). Colloidal metal nanoparticles (MNPs) possess different physical, chemical and optical properties in comparison to their bulk counterpart. For these unique properties, metal nanoparticles have been widely explored in last 30 years for various applications (Li X et al. 2014; Bresee J et al. (2014); Wunder S et al (2011); Alkilany AM et al. (2013); Zhang Y et al. (2012); Fazal S et al. (2014); Murphy CJ et al. (2008); Thomas KG and Kamat PV (2003) and Prati L and Villa A (2014)). Recently, the synthesis of MNPs in aqueous medium by using eco-friendly reducing agents which can act as stabilizing agents also has drawn significant interest not only for reducing the production of hazardous materials but also for many bio-based applications (Ying S et al. (2022); Jadoun S et al. (2021); Gour A and Jain NK (2019) and Anastas PT and Kirchhoff MM (2002)). In this perspective, various plant extracts which contain

significant amount of polyphenols and flavonoids have been widely explored as reducing as well as stabilizing agents for the synthesis of colloidal metal nanoparticles from the corresponding metal salts under mild conditions. The easy availability of various plant parts, cheap rates, no need of additional capping or hazardous reducing agents, make them an attractive alternative precursor for the solution phase synthesis of colloidal metal nanoparticles (Iravani S (2011); KN Thakkar KN (2010); Huang X (2010); Verma RS (2014); Wu H et al. (2011); Reddy J et al. (2015) and Nadagouda MN and Varma RS (2008)). As the leaf extract of Chrysophyllum cainito (LECC) is rich in polyphenols, we utilized this polyphenol rich leaf extract for synthesizing stabilized colloidal gold nanoparticles (AuNPs) from the precursor Au (III) salt in aqueous medium at room temperature. The appearance of pink color in the colorless solution indicated the formation of colloidal gold nanoparticles (AuNPs) via bottom-up approach. The formation of stabilized colloidal gold nanoparticles was initially confirmed by the presence of surface plasmon resonance band (SPR) via UV-visible spectroscopy. The formation of AuNPs was confirmed by X-ray diffraction studies and Fourier transform-infrared spectroscopy (FTIR) studies also. The morphology and size of the synthesized AuNPs were confirmed by high-resolution transmission electron microscopy (HRTEM), Dynamic Light Scattering (DLS), energy dispersive X-ray (EDX) studies. Sodium borohydride (NaBH4) mediated reduction of 3-nitrophenol (3-NP) and 4-nitrophenol (4-NP) at room temperature is not possible due to large kinetic barrier. Interestingly, on addition of C. cainito leaf extract stabilized colloidal AuNPs to the reaction medium, the reduction of the nitrophenols to aminophenols have been observed within few minutes which confirmed the excellent efficacy of the synthesized colloidal nanoparticles as catalyst.

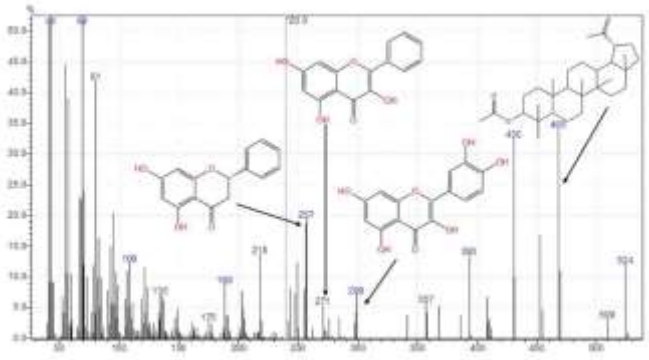


Figure 1: Mass spectrum of Chrysophyllum cainito leaf extract

2. Materials and Methods

Preparation of Au(III) salt solution: $HAuCl_4$ salt was purchased from Sisco Research Laboratory (SRL). A 10.42 mM stock solution of Au(III) salt was prepared by dissolving 35.4 mg $HAuCl_4$ salt in 10 mL double distilled water. The leaves of *Chrysophyllum cainito* were collected from the north-central part of Thailand.

Preparation of the *Chrysophyllum cainito* leaf extract: Dried and finely powdered *Chrysophyllum cainito* leaf (6.0 g) was taken in a conical flask. Then 50 mL methanol was added to the conical flask to make a suspension which was stirred at room temperature for 2 hours. After that the suspension was filtered which yielded greenish filtrate. The filtrate was dried under reduced pressure yielding a greenish crystalline solid (0.974 g). A tiny amount (0.005 g) of greenish crystalline solid (0.005 g) was suspended in distilled water (10 mL). The resulting suspension was sonicated in an ultra sonicator bath for few minutes resulting a semi-transparent solution (500 mgL^{-1}).

Synthesis of colloidal gold nanoparticles (AuNPs): A series of vials containing leaf extract of *Chrysophyllum cainito* with varied concentrations (10, 20, 40, 60, 80, 100, 200 mg L^{-1}) were prepared. Then a small amount of Au (III) solution (0.16 mL, 10.42 mM) was added drop-wise to each vial to synthesize a series of stabilized colloidal AuNPs. In each vial, the final concentration of Au(III) was 0.42 mM. Within few minutes, red color appeared in each vial which indicate the formation of colloidal AuNPs. After 3 hours of addition, UV-visible measurements of each colloidal solution were performed.

Characterization: Transmission electron microscopy of AuNPs was carried out in JEOL 2100 instrument. To study the X-ray diffraction (XRD) patterns of the stabilized AuNPs, we deposited the colloidal AuNPs dropwise on a glass slide and dried it under bulb. On repeated deposition a thin film of AuNPs was prepared which was used to study X-ray diffraction (XRD) patterns. The instrument was Panalytical X'pert Pro diffractometer with Cu-Kα radiation (λ= 1.54 Å). Mass spectral analysis of the *Chrysophyllum cainito* leaf extract was performed in Shimadzu GCMS QP 2100 plus. All the UV-Visible spectroscopic measurements were carried out by using Shimadzu 1601 spectrophotometer. FTIR analysis of all the samples were performed in Perkin Elmer FTIR Spectrum-II model. KBr pellets were prepared with the samples for performing FTIR.

Catalytic activity of synthesized AuNPs in the Sodium borohydride mediated reduction of m- and p- nitrophenol:

1. Experimental Procedure of reduction of 4-nitrophenol to 4-aminophenol: Catalytic reduction of 4-nitrophenol to 4- aminophenol was carried out as follows: (a) initially 0.2 mL of 0.05 mM 4-nitrophenol was taken in a cuvette and diluted to 4 mL with distilled water to record the UV-visible spectrum. (b)Then 0.2 mL of 0.05 mM 4-nitrophenol was again taken into the cuvette. After that 3.6 mL of freshly prepared 15 mM sodium borohydride solution was added to the cuvette and then the volume was made up to 4mL with 0.2 mL of distilled water. UV-visible spectrum of the resulted reaction mixture was recorded. (c) Again 0.2 mL of 0.05 mM 4-nitrophenol was taken into the cuvette and 3.6 mL of freshly prepared 15 mM sodium borohydride solution was added to the cuvette. After that freshly prepared *Chrysophyllum cainito* leaf extract stabilized gold nanoparticles (20 mgL^{-1}/40 mgL^{-1}, 0.2 mL) was added to the cuvette. After shaking the reaction, the UV-visible spectra were recorded at room temperature. The progress of the reactions was monitored by recording the decreasing absorption intensity of 4-nitrophenolate ion with certain time intervals. Based upon the experiment data, the value of the catalytic rate constants were calculated.

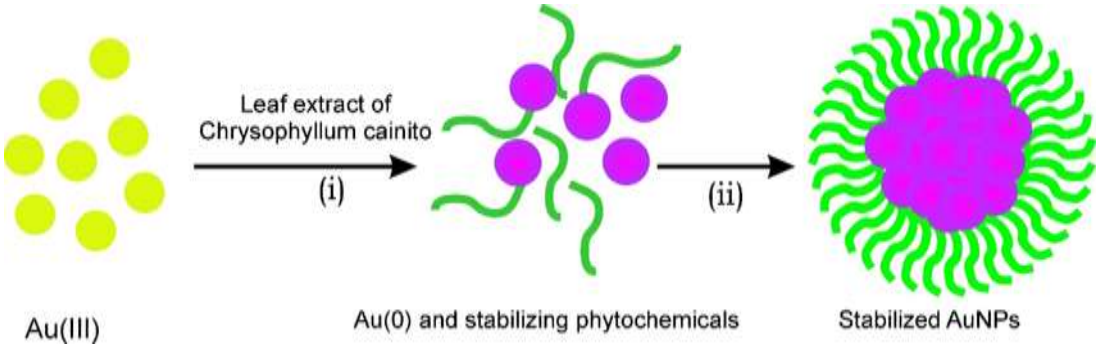
2. Experimental Procedure of the reduction of 3-nitrophenol to 3-aminophenol: Catalytic reduction of 3-nitrophenol to 3- aminophenol was carried out as follows: (a) initially 0.2 mL of 0.05 mM 3-nitrophenol was taken in a cuvette and diluted to 4 mL with distilled water to record the UV-visible spectrum. (b) Then 0.2 mL of 0.05 mM 3-nitrophenol was again taken into the cuvette. After that 3.6 mL of freshly prepared 15 mM sodium borohydride solution was added to the cuvette and then the volume was made up to 4mL with 0.2 mL of distilled water. UV-visible spectrum of the resulted reaction mixture was recorded. (c) Again 0.2 mL of 0.05 mM 3-nitrophenol was taken into the cuvette and 3.6 mL of freshly prepared 15 mM sodium borohydride solution was added

to the cuvette. After that freshly prepared *Chrysophyllum cainito* leaf extract stabilized gold nanoparticles (20 mgL^{-1}, 0.2 mL/0.05 mL) was added to the cuvette. After shaking the reaction, the UV-visible spectra were recorded at room temperature. The progress of the reactions was monitored by recording the decreasing absorption intensity of 3-nitrophenolate ion with certain time intervals. Based upon the experiment data, the value of the catalytic rate constants were calculated.

3. Results

Proposed mechanism for the synthesis of stabilized colloidal AuNPs by LECC:

Literature studies revealed that the leaves of C. cainito is a rich source of flavonoids, phenols, sterols and terpenoids (Das A et al. (2010); Koffi N et al. (2009); Shailajan S and Gurjar D (2014) and Meira NA et al. (2014)). A ferric chloride test has been done to confirm the presence of polyphenolic compounds in the C. cainito leaf extract. Instant color change confirmed the presence polyphenolic compounds. Mass spectral analysis has been done the leaf extract of Chrysophyllum cainito which supported the presence of pinocembrine (M+ 257), galangin (M+ 271), quercetin (M+ 299), lupeol acetate (M+ 468), lupeol hexanoate (M+ 524) etc. (Shailajan S and Gurjar D (2014) and Sultana R et al. (2021)) (Figure 1).



Scheme 1. Schematic representation for the synthesis of stabilized colloidal AuNPs by the leaf extract of Chrysophyllum cainito.

Literature studies revealed that the polyphenolic compounds can make chelate complex with the positively charged metal ions via coordination bonds. Then the positively charged metal ions were reduced to metal (0) by the chelating agent polyphenols with concomitant oxidation of the polyphenols. The synthesized metal (0) atoms then collide to each other to come into the nano range which were then stabilized as metal nanoparticles (MNPs) by the carbonyls of quinone molecules along with the free hydroxyls which inhibit the coagulation of individual particles (Ferrer M et al. (1999) and Wu H et al. (2011)). As the leaf extract of *C. Cainito* contains significant amount of polyphenolic compounds, we propose a probable mechanism for the synthesis of stabilized AuNPs by using LECC extract as shown schematically in Scheme 1.

Synthesis of stabilized colloidal gold nanoparticles (AuNPs) by utilizing leaf extract of Chrysophyllum cainito:

Stabilized gold nanoparticles (AuNPs) have been synthesized by reducing Au(III) salts with LECC at room temperature. The synthesized colloidal AuNPs are stable enough which indicated excellent efficacy of LECC as stabilizing agent. The synthesized

colloidal AuNPs were characterized by UV-visible spectroscopy where characteristic intense surface plasmon resonance band (SPR) band were observed in the region of 524 - 534 nm (Figure 2) [**Error! Bookmark not defined.**]. Hypsochromic shift was observed on increasing the concentration of stabilizing agent LECC from 10 mgL^{-1} to 200 mgL^{-1} which indicated the formation of relatively smaller sized AuNPs with higher concentration of stabilizing agent due to better stabilization. During the reduction of Au(III) to Au (0) by polyphenolic compounds of LECC, the polyphenolic compounds were concomitantly oxidized to quinones which was confirmed with a broad peak at 270–275 nm region in the spectrum of AuNPs.

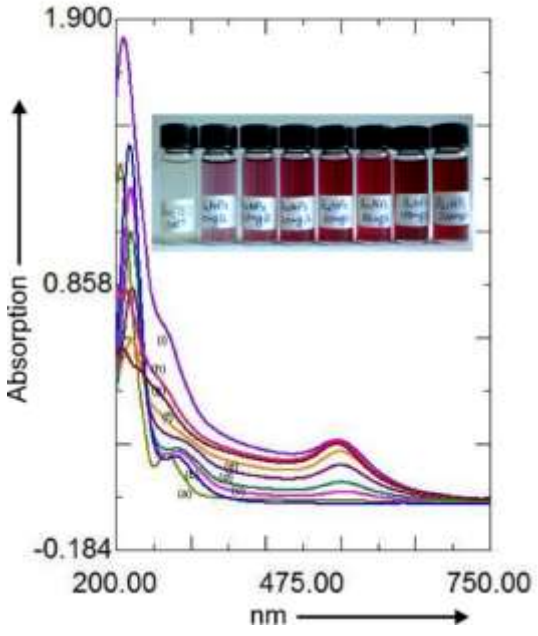


Figure 2. UV-Visible spectra of: (a) Plant extract (100 mgL^{-1}), (b) $HAuCl_4$ (0.42 mM), (c-i) AuNPs at 10, 20, 40, 60, 80, 100, 200 mgL^{-1} concentrations of LECC, respectively. Inset: Photograph of Au (III) solution and stabilized AuNPs with 10, 20, 40, 60, 80, 100, 200 mgL^{-1} concentrations of LECC. The photograph was taken after 18 hours of synthesizing AuNPs.

Dynamic Light Scattering (DLS) measurement was carried out with colloidal AuNPs stabilized with 10 mgL^{-1} to 80 mgL^{-1} LECC which revealed that 30-33 nm is the average hydrodynamic diameter range. On further increasing the concentration of LECC (100 mgL^{-1} and 200 mgL^{-1}), the hydrodynamic diameter range of stabilized AuNPs enhanced from 30 to 50 and 100 nm respectively (Figure 3). As DLS provide details of the whole conjugate, in the presence of higher concentration of LECC as stabilizing agent, an enhancement in the size of stabilized AuNPs was observed due to the presence of more stabilizing agents on the surface of synthesized AuNPs. High negative values of Zeta Potential of synthesized AuNPs are responsible for the stability of the synthesized colloidal AuNPs by preventing the agglomeration of the nanoparticles (Table 1) (Iravani S (2011).

High resolution transmission electron microscopy (HRTEM) technique has been used to determine the size and morphology of the synthesized AuNPs. At higher concentration (100 mgL^{-1}) of LECC, discrete AuNPs with average size 14-16 nm were observed which were spherical in majority (Figure 4). At lower concentration of LECC (60 $mg.L^{-1}$), assembled AuNPs were observed which had similarity with flowers (Figure 5). At lower concentration of LECC, due to the presence of less number of stabilizing agents at surface, the AuNPs assembled together which yielded flowerlike structures. The presence of organic matrix where the synthesized AuNPs were embedded was evident from Figure 5a (shown by arrow). At high resolution of HRTEM, lattice fringes of a single AuNP was observed which has an interplanar d-spacing of 0.15 nm (Figure 6). This d-spacing value is in agreement with the d-spacing value of (220) plane of a face centered cubic crystalline.

Table 1: Zeta Potential values of the stabilized AuNPs:

Serial No.	AuNPs Samples	Zeta Potential (mV)
1.	AuNPs (synthesized and stabilized with 200 mg/L LECC)	-27.4
2.	AuNPs (synthesized and stabilized with 100 mg/L LECC)	-29.5
3.	AuNPs (synthesized and stabilized with 80 mg/L LECC)	-28.2
4.	AuNPs (synthesized and stabilized with 60 mg/L LECC)	-31.5
5.	AuNPs (synthesized and stabilized with 40 mg/L LECC)	-30.5
6.	AuNPs (synthesized and stabilized with 20 mg/L LECC)	-30.8
7.	**AuNPs (synthesized and stabilized with 10 mg/L LECC)**	**-29.5**

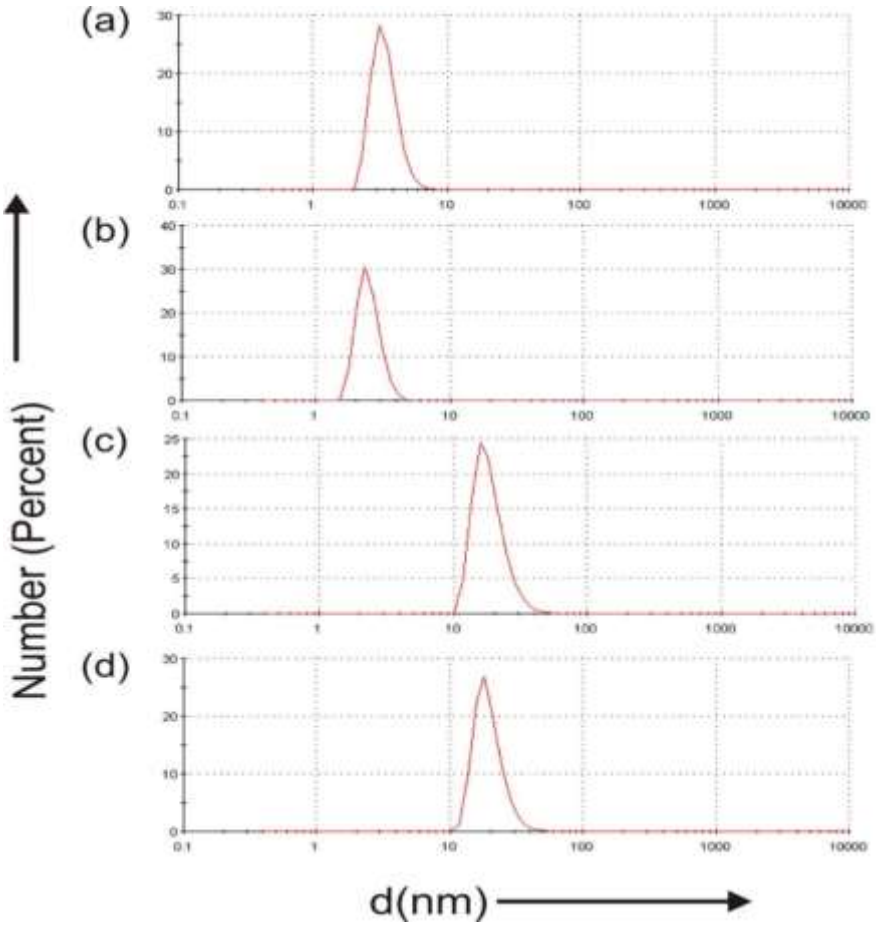


Figure 3. Particle size distribution of the stable colloidal AuNPs synthesized and stabilized with LECC at the concentration of (a) 10 mgL^{-1}, (b) 40 mgL^{-1}, (c) 60 mgL^{-1}, (d) 100 mgL^{-1} .

Au (JCPDS file no. 04-0784). Energy Dispersive X-ray (EDX) analysis was performed for the synthesized dried colloidal AuNPs which confirmed the presence of gold as well as carbon and oxygen (Figure 5e). Sharp peak of carbon and oxygen confirmed the presence of LECC as stabilizing agent on the surface of synthesized AuNPs. Selected Area Electron Diffraction (SAED) pattern was determined from AuNPs which yielded the diffraction rings (from inner to outer) associated with the (111), (200), (220) and (311) atomic planes of Au which are in agreement with the plane of crystalline gold (Figure 5f). X-ray diffraction analysis of the dried film of synthesized colloidal AuNPs yielded characteristic reflections of the planes (111), (200), (220) and (311) at 2θ = 38.5°, 44.9°, 65.3° and 78.2°, respectively which are in agreement with the value of metallic face centered cubic (fcc) Au (Figure 7, Table 2**)**, (JCPDS file no. 04-0784).

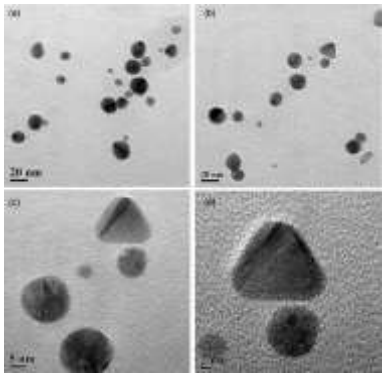


Figure 4. (a-d) HRTEM images of colloidal nanoparticles with 100 mgL^{-1} leaf extract at different magnification.

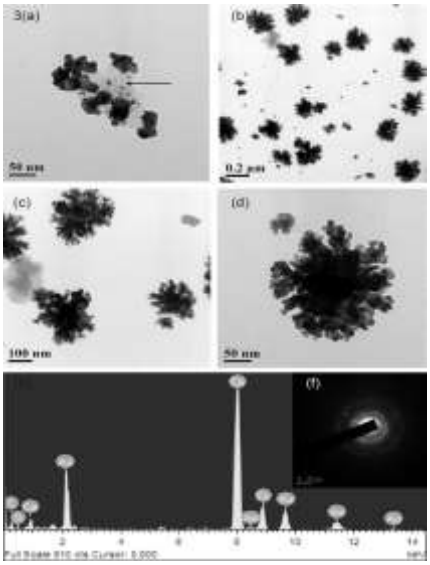


Figure 5. (a-d) HRTEM images of AuNPs synthesized and stabilized with 60$mg.L^{-1}$ LECC ; (a) Initiation of the assembly of the discrete nanoparticles are shown by arrow, (b) At low magnification, assembled AuNPs looked like flowers, (c,d) At higher magnification, images of two different assembled AuNPs looked like flowers. magnification. (e) Elemental analysis of dried colloidal AuNPs by Energy dispersive X-ray (EDX) and (f) SAED pattern of an AuNP.

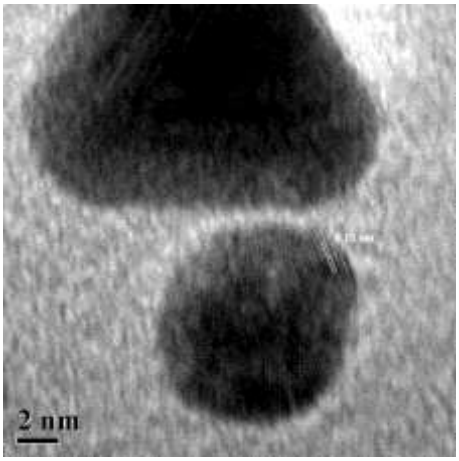


Figure 6: HRTEM image of AuNP synthesized and stabilized with 100mgL^{-1} LECC showing the lattice fringes with d- spacing 0.15 nm.

Table 2: 2θ and the corrosponding d values obtained from the X-ray diffraction of the dried film of colloidal AuNPs synthesized and stabilized with LECC.

2 Theta(degree)	d (Å)	Corresponding hkl plane
38.51	2.3355	111
44.87	2.0185	200
65.25	1.43	220
78.16	1.22	311

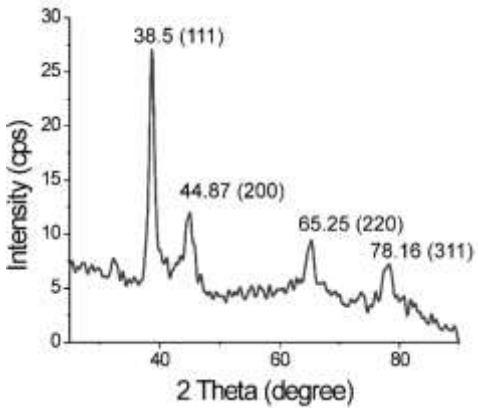


Figure 7: X-Ray Diffraction Pattern of the dried film of synthesized colloidal AuNPs stabilized with LECC.

The FTIR study is an important tool to investigate the role of different functional groups of available biomolecules in LECC for synthesizing and stabilizing the AuNPs. For this purpose FTIR have been performed with both solid LECC and dried colloidal AuNPs (Figure 8). A broad peak around 3382 cm^{-1} was observed in solid LECC sample due to the stretching vibration of the aliphatic and aromatic hydroxyl groups present in the polyphenols of LECC (Figure 8a). The broad nature of the peak indicated the presence of intermolecular hydrogen bonding between the hydroxyl groups. The presence of peaks in the 1614 - 1400 cm^{-1} range (1614, 1539, 1449 cm^{-1}) also supported the presence of aromatic rings in the phytochemicals. The peak at 1365 cm^{-1} is indicated the in plane bending of the OH

groups (Figure 8a). Interestingly, for the AuNPs stabilized by the phytochemical derivatives of LECC, the stretching vibration at 3436 cm^{-1} for the aliphatic and aromatic OH groups became narrower and shifted to the higher frequency region which is an indication of weakening of the intermolecular H-bonding (Figure 8b). In addition, weakening of the in-plane bending frequency of OH group at 1365 cm^{-1} was also observed in case of the stabilized AuNPs by LECC (Figure 8b).

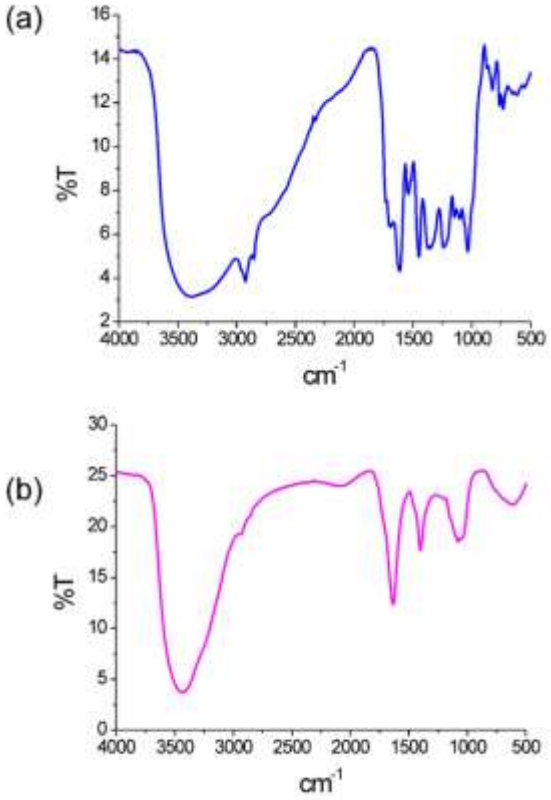


Figure 8: FTIR spectra of (a) *LECC* and (b) *LECC* stabilized AuNPs.

Chrysophyllum cainito leaf extract stabilized colloidal AuNPs: An effective catalyst for reduction reaction.

To investigate the catalytic efficacy of the LECC stabilized colloidal AuNPs, we have chosen sodium borohydride mediated model reduction reactions which could be performed in water medium at room temperature (Verma RS, 2014). Initially, the absorption band of aqueous 4-nitrophenol was measured at 318.5 nm. After the addition of sodium borohydride, the band was shifted to longer wavelength (400 nm) with significant enhancement of the absorption intensity. Due to large kinetic barrier for the reduction reaction, no further change was observed at room temperature though the reduction reaction is thermodynamically favourable (E_0 for 4-nitrophenol/4-aminophenol is -0.76 and for H_3BO_3/BH_4^- is -1.33 V). On addition of colloidal AuNPs (0.2 mL, synthesized and stabilized with 20 mgL^{-1} LECC) to the reaction mixture, a gradual decrease of the absorption intensity at 400 nm was observed which was completely disappeared within 13 minutes. At the same time, a new peak appeared at around 300 nm which confirmed the transformation of 4-nitrophenolate to 4-aminophenol (Figure 9I-II). During this reaction, the colour change of the reaction mixture was visually observed where the greenish yellow colour of the reaction mixture faded within few minutes after the addition of the colloidal AuNPs as catalyst. This reaction is considered as pseudo 1^{st} order reaction because the concentration of BH_4^- was approximately 300 fold higher than the concentration of p-nitrophenol. The rate constant (k) of this pseudo 1^{st} order reaction was calculated as 0.25 min^{-1} (Table 3 and Figure 10b) [26]. In the presence of colloidal AuNPs as catalyst, both 4-nitrophenol and BH_4^- ions are adsorbed on the surface of the AuNPs. As a result, easy hydride transfer is possible from BH_4^- to the 4-nitrophenol which facilitated the reduction reaction (Wunder S 2011; Murphy CJ ; 2008; Wu H 2011). When equal volume (0.2 mL) of colloidal AuNPs synthesized and stabilized with 40 mgL^{-1} LECC was used for the reduction reaction, then the reduction rate was comparatively slow and was completed in 25 minutes. This is perhaps due to the

presence of larger amount of stabilizing agent on the AuNP surfaces which hindered both the 4-nitrophenolate ion and BH_4^- ion to be absorbed on the surface. With increasing volume of AuNP as catalyst, as large number of reaction sites were present in the reaction mixture, the hydride transfer process became easier which leaded the enhancement of the reduction reaction rate.

Similar experiment was performed with 3-nitrophenol also. An aqueous solution of 3-nitrophenol has shown an absorption band at 330 nm. On addition of freshly prepared sodium borohydride, the peak at 330 nm was shifted to the longer wavelength region (390 nm) with a significant absorption intensity enhancement due to the formation of more stable 3- nitrophenolate ion (Figure 9III). However, no further change was observed for several hours. Interestingly, on addition of colloidal AuNPs (0.2 mL, synthesized and stabilized with 20 mgL^{-1} LECC) to the reaction mixture, the peak at 390 nm was disappeared almost instantly. At the same time, a new peak at around 300 nm appeared. On addition of $1/4^{th}$ volume of stabilized AuNPs (0.05 mL, synthesized with 20 mgL^{-1} LECC) to the 2^{nd} set of reaction mixture under same condition, the intensity of absorption peak at 390 nm started to decrease with the time and it took 15 minutes for the complete disappearance of the peak. From the data of this reaction, the rate constant (k) was calculated as 0.17 min^{-1} (Figure 9 IV, Table 3 and Figure 10a).

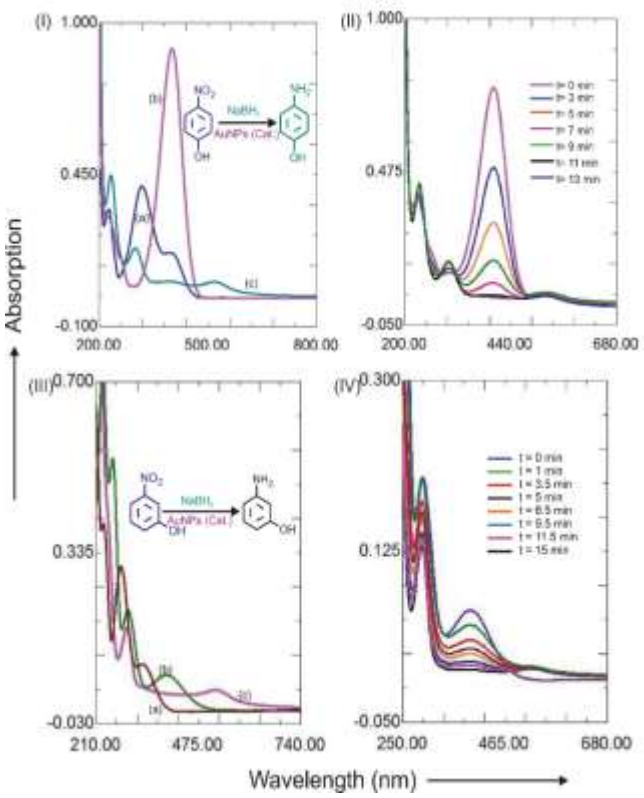


Figure 9: (I) UV-visible spectra of: (a) 0.05 mM 4-nitrophenol, (b) after addition of 15mM sodium borohydride into the 4-nitrophenol solution, (c) Complete transformation of 4-nitrophenolate into 4-aminophenol after adding 0.2 mL of colloidal AuNPs as catalyst. (II) UV- visible spectra at different time intervals during monitoring the $NaBH_4$ mediated reduction of 4-nitrophenol to 4-aminophenol by using 0.2 mL of colloidal AuNPs (stabilized with 20 mgL^{-1} LECC) as catalyst. (III) UV–visible spectra of: (a) 0.05 mM 3-nitrophenol, (b) after addition of 15mM sodium borohydride into the 3-nitrophenol solution, (c) Complete transformation of 3-nitrophenolate into 3-aminophenol within 1 minute after addition of 0.2 mL colloidal AuNPs stabilized with LECC as catalyst. (IV) UV-visible spectra at different time intervals during monitoring the $NaBH_4$ mediated reduction of 3-nitrophenol to 3-aminophenol using 0.05 mL colloidal AuNPs (stabilized with 20 mgL^{-1} LECC) as catalyst.

Table 3. Efficacy of the colloidal AuNPs (synthesized and stabilized with LECC) as catalyst for the $NaBH_4$ mediated reduction of nitrophenols to aminophenols.

Nitrophenol(NP) (mM)	sodium borohydride (mM)	Colloidal AuNPs (mL)	Reaction completion time (min)	Catalytic rate constant(k) (min^{-1})
4-NP/0.05	13.5	0.2(40 $mg.L^{-1}$)	25	0.1
4-NP/0.05	13.5	0.2(20 $mg.L^{-1}$)	13	0.25
3-NP/0.05	14.1	0.05(20 $mg.L^{-1}$	15	0.17
3-NP/0.05	13.5	0.2(20$mg.L^{-1}$)	1	Can't be calculated
3-NP/4-NP/0.5	13.5	0.0	No reduction	-
3-NP/4-NP/0.5	0.0	0.2	No reduction	-

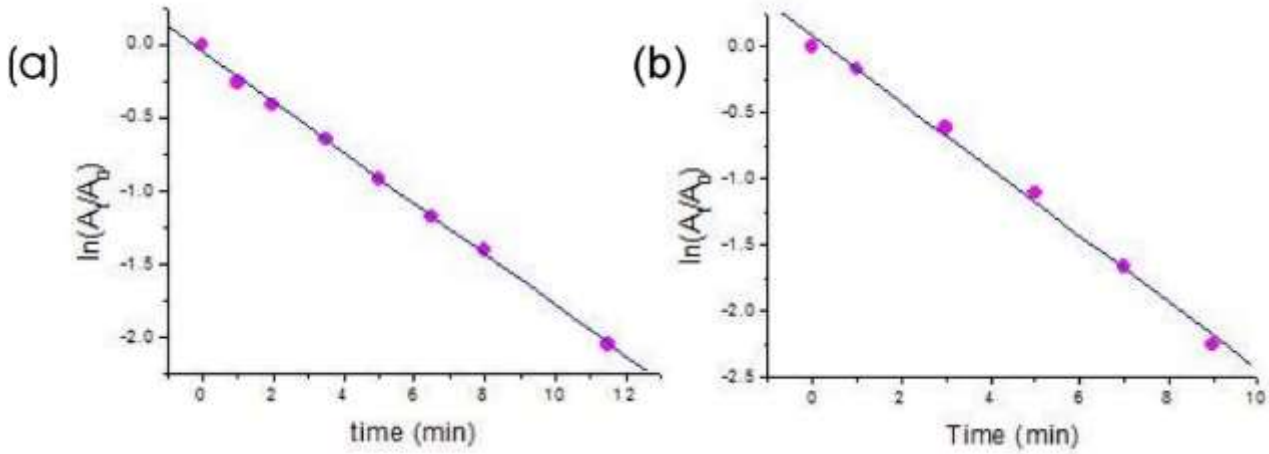


Figure 10: ln (A_t/A_0) vs time plot of: (a) $NaBH_4$ mediated reduction of 3-nitrophenol in presence of 0.05 mL colloidal AuNPs (stabilized with20 mgL^{-1} LECC) as catalyst, (b) $NaBH_4$ mediated reduction of 4-nitrophenol in presence of 0.2 mL colloidal AuNPs (stabilized with 20 mgL^{-1} LECC) as catalyst. From the slope of the graphs, the catalytic rate constants (k) were calculated as 0.17 min^{-1} in (a) and 0.25 min^{-1} in (b).

4. Conclusion

A very simple method for the synthesis of colloidal gold nanoparticles from HAuCl4 solution has been reported at room temperature under very mild condition where the leaf extract of C. cainito was utilized as reducing as well as stabilizing agent. According to our knowledge, this is the first report for the synthesis of colloidal AuNPs utilizing the leaf extract of C. cainito. This environmentally benign method described here is very cost effective as well as less hazardous. As the leaf extract of C. cainito is a rich source of polyphenolic compounds, these polyphenols can easily reduce Au (III)

to Au (0) via chelate complex formation with the concomitant oxidation of the polyphenols into quinones. Then these quinone moieties, remaining polyphenols and other phytochemicals present in the leaf extract of C. cainito play an efficacious role to stabilize the synthesized colloidal AuNPs. From the HRTEM analysis, it is evident that at lower concentration of the leaf extract, the flower-like assemblies of nanoparticles were formed, whereas at higher concentration of the leaf extract, discrete nanoparticles were formed. Considering the huge significance of aminophenols in pharmaceutical, photographic and chemical dye industries as important precursors and synthetic intermediates, the efficacy of the synthesized colloidal gold nanoparticles as catalyst have been checked for the sodium borohydride mediated reduction of 3- and 4-nitrophenol at room temperature. The progress of both reactions were monitored by UV-visible spectroscopy with time which confirmed the efficacious role of synthesized colloidal AuNPs as catalyst.

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