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Green synthesis of silver nanoparticles with Bhara gum: characterizationand catalytic reduction of para nitrophenol

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Abstract: Silver nanoparticles (AgNPs) were synthesized using aqueous bhara gum and the gum act as a reducing agent and stabilization agent. The synthesized silver nanoparticles were characterized by UV-Visible Spectrophotometer, Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD), Transmission Electron Microscopy (TEM). The characterization results confirmed the formation of silver nanoparticles and were crystalline nature. The average sizes of synthesized nanoparticles are 12±3 and hydroxyl and carbonyl groups are responsible for the reduction and stabilization. The green synthesized silver nanoparticles were studied for their catalytic activity for the reduction of para nitrophenol in the presence of a reducing agent, $NaBH_4$.The kinetics of the reaction was found to be ofpseudo-first-order with respect to the 4-NP.Thus, the synthesized new gum-based catalyst was found very efficient, stable, cost-effective, easy to prepare and eco-friendly.

Key words: Silver nanoparticles, Bhara-gum, green synthesis, catalytic activity.

Introduction

In the present day's nano particles plays a major role in science and technology due to their unique size, shape, peculiar properties and potential applications [1]. Among the several metal nano particles, silver nanoparticles have attracted rigorous consideration of their numerous applications in sensing, catalysis, magnetic, tunable surface plasmon resonance, and bio stability and anti-bacterial activity [2-4]. Most of the available methods for the synthesis of silver nano particles involve chemical reduction, photo chemical reduction and electrochemical reduction [5,6]. The reagents can be inorganic compounds such as Na/KBH_4, salts of tartrate, organic compound like sodium citrate and ascorbic acid which are capable of being oxidized [7]. However, it needs to be avoidable the use of chemical reagents in the AgNPs which are ecologically injurious.Hence, non ecofriendly nature of the chemical methods has the inherent drawbacks [8]. The replacement of non-ecofriendly synthesis methods with nontoxic,clean and globally acceptable green chemistry methods are the present day need in synthesizing AgNPs [9]. Several biological systems such as fungi, bacteria and plants can actively reduce metal ions and form eco-friendly nano particles. Among these, gums extracted from plants such as tragacanth gum, gum Arabic and chitosan etc., which are natural polymers, act as reducing agents and stabilizing agents [10,11].

Bhara gum, a yellowish natural gum, is available from the bark of Terminalia bellerica. This gum is basically cost effective, easily available, non-toxic and has a potential application as a food additive. Main chemical components are tannins which mainly include gallic acid, galloyl glucose,ß-sitosterol, ellagic acid, ethyl gallate, and chebulaginic acid. Bhara gum was used in drug delivery, microcapsules were formulated by ionic gelation technique using famotidine as the model drug. Carboxylic acid, acetyl, hydroxyl and carbonyl groups are identified as major functional groups in the gum [12].

Silver in the form of nanoparticles shows excellent catalytic activity towards several chemical reactions. Nitro phenols are environmental toxic substance due to their poisonousness and inhibitory nature. In addition, Nitro phenols have vastly solubility and stability in water. Due to this reason the reduction of 4-NP in to 4-AP is prominent. Sodium borohydride is a very strong reducing agent, but, it has no ability to reduce the Nitro phenol. $NaBH_4$ is not effective in this reaction except provided with some catalyst to reduce the kinetic barrier of the reaction. A variety of catalysts were used in the past and, recently, Pt, Au nanoparticles have been used for the same purpose [13-15].

In this study the green synthesis of silver nano particles made by bhara gum is a core subject. This gum acts as a reducing and stabilizing agent. We studied the synthesis of AgNPs and their characterization by UV-Visible spectrophotometer, FTIR, XRD and TEM. AuNPs were explored with respect to their prospective catalytic applications.

2. Experimental section

2.1 Materials

Silver nitrate ($AgNO_3$, 99.9%) was purchased from sigma Aldrich, and sodium borohydride ($NaBH_4$, 98%), nitric acid (HNO_3), hydrochloric acid (HCl) and p-nitro phenol (PNP) were purchased from S-D Fine chemicals. Bhara gum was purchased from Girijan Co-operative Corporation Limited.

2.2 Method

In the synthesis of AgNPs all the glassware were washed with aquaregia (3:1HCl-HNO3) and then thoroughly rinsed with deionized water. All the solutions were prepared in milli-qwater. 1ml of 1% $AgNO_3$ solution and gum solution (3ml) were mixed within a boiling tube. This reaction mixture was kept in an autoclave at 15 psi pressure and 120^0c for 10 minutes. The resulting solution was yellow colorindicating the formation of silver nano particles.

2.3 Catalytic reduction of p-nitrophenol

As a sample reaction, we selected the reduction of p-nitro phenol by sodium borohydride to p-aminophenol. The reduction took place in aqueous solution in a standard quartz cell with a 1cm path length. The reaction process is as follows: 1.5 mL of 0.2mM p-nitro phenol was mixed with 1.2 mL of 0.015M NaBH4 in the cell for UV-Visible measurements. Immediately, the color changed from light yellow to deep yellow. 100 µL of AgNPs solution was added to the above mixture. The UV-Visible absorption spectra were recorded with a time interval in a scanning range of 200-700nm [16].

3. Characterization

3.1 UV Visible

In order to study the silver nano particles, the UV–Visible absorption spectra of the prepared colloidal solution was recorded using a UV-Vis-NIR Spectrophotometer (UV-3600, shimadzu).

3.2 FTIR

A pure KBr pallet used as background this was subtracted from the FTIR spectra of the bhara gum and AgNPs sample. The scan was done in the range of 400–4000cm−1. FTIR spectra were recorded with an instrument IRAffinity-1 (Shimadzu).

3.3 TEM& XRD

The morphologies of products were studied by a transmission electron microscopy (TEM). The sample girds for TEM measurements were prepared by placing a drop of aqueous AuNPs dispersion on the copper girds and subsequently evaporating water naturally overnight at ambient condition. The size of the AuNPs was determined by a JEOL 2000 FX-II TEM. The crystallinity of the AuNPs was studied by XRD (rigaku, miniflex) with Cuka radiation.

4. Results and Discussion:

4.1 UV-Visible spectroscopy

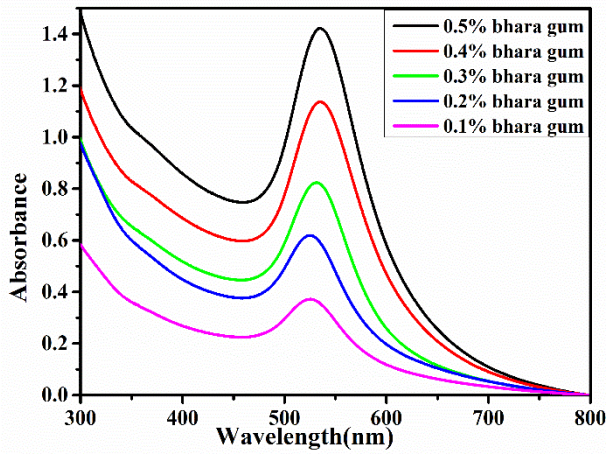

Fig. 1. The UV–Vis absorption spectra of AgNPs synthesized by autoclaving different concentrations of bhara gum solution with 0.5% $AgNO_3$.

Silver nano particles formation was primarily observed by UV-Visible spectroscopy. The color change is attributed to the Surface Plasmon Resonance (SPR). A characteristic SPR band for AuNPs is obtained at around λ 410- 435nm. The part of gum concentration on the synthesis of nanoparticles was studied using autoclaving varying the concentrations (0.1to 0.5%) of gum solutions containing 0.5 % of $AgNO_3$ for 15 min (Fig 1). With an increase in gum concentration there was an enhancement in the nanoparticles synthesis. The synthesis was also assessed by varying the concentration of $AgNO_3$ and reduction was studied with 0.5% gum (Fig 2).It tells that the efficiency of nanoparticle synthesis augments with increasing concentration of $AgNO_3$.

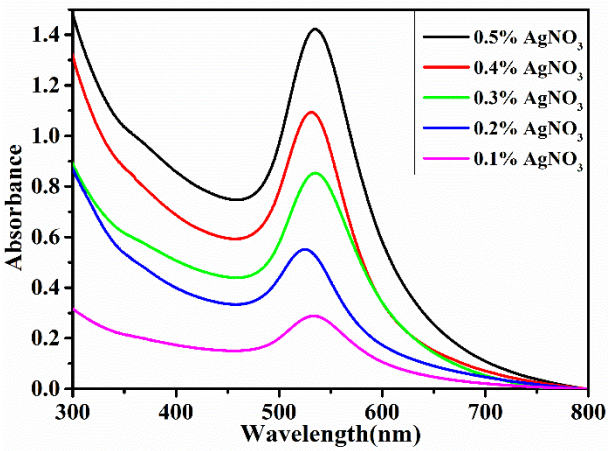

Fig. 2. The UV–Vis absorption spectra of AgNPs synthesized by autoclaving different concentrations of $AgNO_3$ with 0.5 % bhara gum solution.

4.2 FTIR

FTIR analysis was carried out to identify the possible functional groups in the reduction of Ag^+ ions and capping of the reduced nanoparticles synthesized by the aqueous extract of Bhara Gum. Figure 3 (a) and (b) indicate the FTIR spectra of bhara gum and bhara gum capped silver nanoparticles respectively.

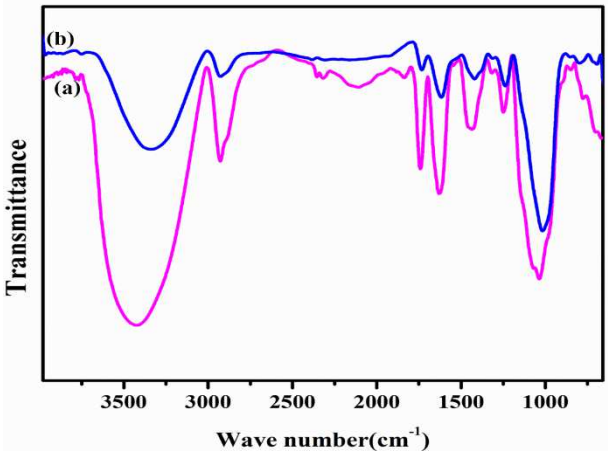

Fig. 3FTIR spectra of (a) bhara gum, (b) AgNPs stabilized in bhara gum.

The major stretching frequencies present in the spectrum of bhara gum are observed at 3328, 2895,1706,1602, 1410,1149 and 1067 cm^{-1}(curve (a) of figure 3), while the bhara gum capped silver nanoparticles showed characteristic stretching frequencies are observed at 3360,2896, 1733, 1595,1432,1140 and1031 cm^{-1} (curve (b) of figure 3). The bonds observed at 3328 suggesting –OH ,2895 asymmetric C-H stretch,1706 carbonyl stretching vibration ,1602 asymmetric stretch of carboxylate , 1410 symmetrical stretch of carboxylate ,1149 and 1067 C-O stretching

vibration of ether and alcohol groups. A shift in the peaks of the FTIR spectrum of gum kondagogu capped AuNPs was observed from 3328 to 3360 cm^{-1},1602 to 1595 $cm^{-1}$and 1410 to 1432 cm^{-1} suggesting the binding of silver nanoparticles with hydroxyl and carboxylate groups remaining peaks are unchanged. Based on the bond shift in the hydroxyl and carboxyl group it can be inferred that both hydroxyl and carbonyl groups of gum are involved in the synthesis and stabilization of silver nanoparticles [16].

4.3 XRD

X-ray Diffraction analysis confirmed the existence of crystalline silver nanoparticles in the sample. The Bragg's reflections observed in the XRD pattern at 2θ 38.10, 44.16, 64.37, and 77.51 which were indexed as the (111), (200), (220), (311) reflections of crystalline metallic silver respectively were Shown in **Fig. 5**. Sharp lines in the XRD pattern indicate the crystalline nature of the synthesized silver nanoparticles.

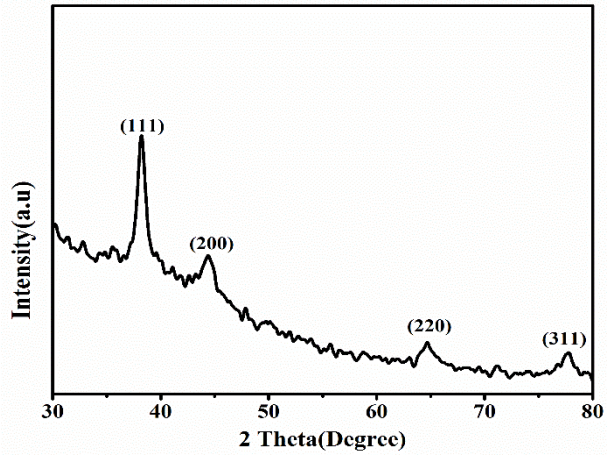

Fig. 4. XRD pattern of synthesized silver nanoparticles.

4.4 TEM

The shape, size, morphology and distribution of the AuNPs were analysed using TEM. Fig. 5 shows that AgNPs synthesized, were predominantly spherical shapes. Histogram constructed by considering 155 nanoparticles suggests that the average size distribution is 12±3 nm.

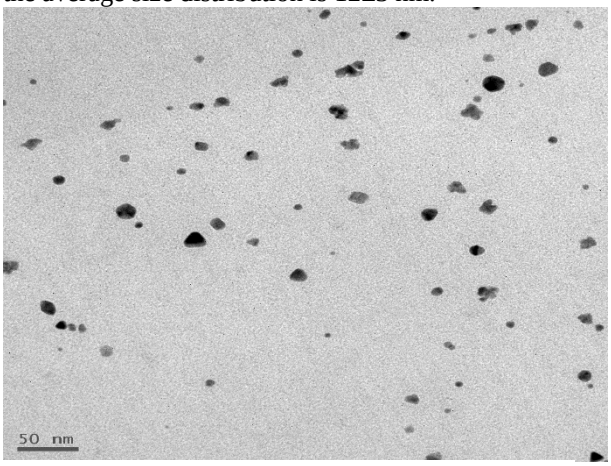

Fig.5 TEM image of synthesized silver nanoparticles.

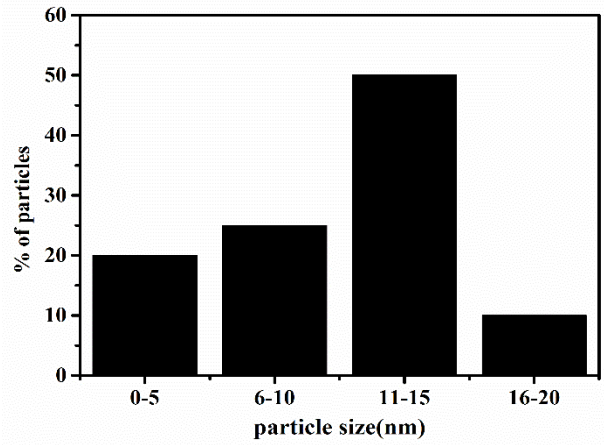

Fig.6. Histogram of synthesized silver nanoparticle.

4.5 Catalytic property

A potential application of silver nano particles is the catalysis of certain reactions that would not otherwise occur. In this study, we have taken a model reduction reaction of p-Nitro phenol (4-NP) to p-Aminophenol (4-AP) by $NaBH_4$. The reduction reaction of 4-NP occurred in aqueous solution in a standard quartz cell with a 1 cm path length. The reaction took place after mixing 1.7 ml of 0.2mM 4-NP with 1ml of 15mM NaBH4 in the quartz cell leading to the change of color from light yellow to deep yellow color. 4-NP solution exhibits a strong absorption peak at 317nm. After the addition of $NaBH_4$, the reaction mixture shows a strong absorption peak at 400nm due to the formation of P- Nitrophenolate ion.

The reduction of 4-NP to 4-AP using aqueous $NaBH_4$ is thermodynamically favorable (E0 for 4-NP/4-AP= -0.76V and H_3BO_3/BH4- = -1.33V versus NHE). The presence of the kinetic barrier due to the large potential difference between donor and acceptor molecules decreases the feasibility of this reaction. There was no change of the peak at 400nm. This indicates that $NaBH_4$ itself was not able to reduce p-Nitrophenolate ion directly. AuNPs were added to phenolate ion mixture and were placed in UV-Visible spectrophotometer. The reaction was followed for every 1-min interval in the range of 200nm to 600nm.

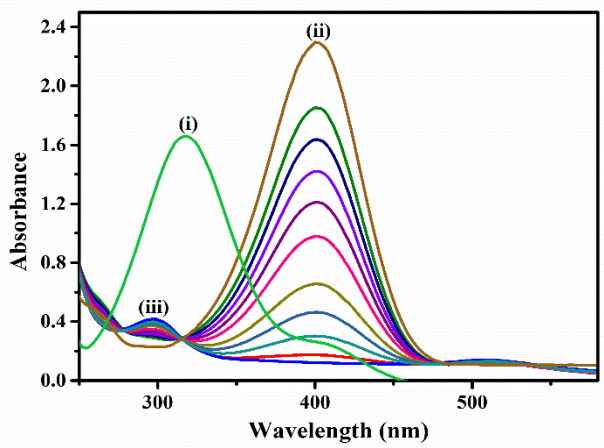

Fig. 7. UV–Visible spectra recorded during the reduction of 4-NP with $NaBH_4$ catalyzed by AuNPs (i) 4-NP,(ii) reduction of nitrophenolate ion with time interval of 1 min, (iii) 4-AP.

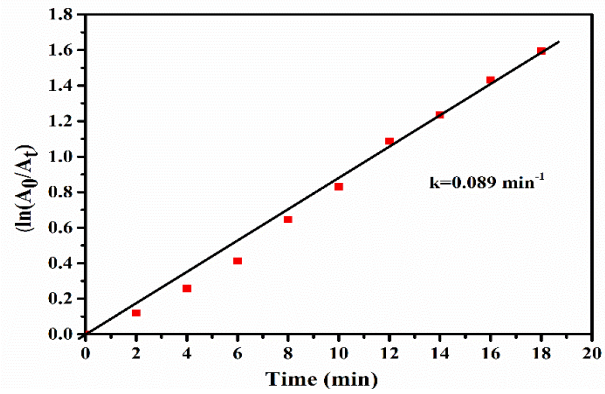

Fig. 8. The plot of $\ln(A_0/A_t)$ versus time for the reduction of 4-NP to 4-AP.

A decrease in the intensity of the absorption peak at 400nm was observed while there is a concomitant appearance of a new peak at 298nm, indicating the formation of reduced product 4-AP.The rate constant of the reaction is of pseudo first order with respect to 4-NP.The concentration of $NaBH_4$ greatly exceeds that of 4-NP, the reaction rate can be assumed to be independent of $NaBH_4$ concentration. The rate constant (k) was determined from the linear plot of ln (A_0/A_t) versus reduction time in minutes.

Conclusion:

Silver nanoparticles have been green synthesized from bhara gum in an ecofriendly route. The synthesis was carried out in an aqueous medium treated by autoclaving using bhara gum as a reducing and capping agent without using any harsh, synthetic reducing.The synthesized nanoparticles were characterized by XRD which confirmedthe face-centred cubic crystalline phase.TEM results shown that the average size of synthesized AuNPs was around 12±3 nm. The catalytic activity of green synthesized AgNPs were evaluated by the hydrogenation of 4-NP reaction.The kinetics of the reaction was found to be of pseudo-first-order with respect to the 4-NP.

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