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BUTEAMONOSPERMA GUM MEDIATED MICROWAVE SYNTHESIS OF GOLD NANOPARTICLES AND THEIR CATALYTIC ACTIVITY

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Abstract
The present study aim to establish a novel green route for the rapid synthesis of gold nanoparticles (AuNPs) using *Buteamonosperma* gum (BMG) by microwave irradiation method. Here the BMG act as a reducing as well as a stabilizing agent. Synthetic conditions such as concentration of BMG, concentration of gold ions (Au^{3+}) and microwave irradiation time were optimized to get the best AuNPs. Prepared AuNPs were thoroughly characterized using UV-Visible, FTIR spectroscopy, XRD and TEM. The UV-Vis spectrum of AuNPs shows a Surface Plasmon Resonance peak at 525 nm. XRD studies indicate that synthesized AuNPs are crystalline innature and TEM revealed spherical shapes with an average particle size of 12±2 nm. Furthermore the synthesized AuNPs exhibited good catalytic activity for the reduction of p-Nitrophenol (4-NP) to p-Aminophenol (4-AP) in the presence of $NaBH_4$. The antibacterial activity of synthesized AuNPs are studied against four bacteria. AuNPs shows positive antibacterial activity against klebisellapneumonia and negative antibacterial activity against stayphylococusaureoous,basilusbtilis andEscharesiacoli.

Keywords: green synthesis, microwave, p-nitrophenol, gold nanoparticles, gum.

Introduction

In recent years, nanoparticles have attracted tremendous attention due to their excellent applications in several fields such as biomedical, sensing, catalysis, food, optics and fuel cells[i]etc. In these context metal nanoparticles has interesting features that have shape and size dependent reactivity due to the increase of volume to surface ratio. Among several metal nanoparticles especially gold nanoparticles (AuNPs) are found suitable candidates in applications such as drug delivery system, sensing and catalysis[ii]. Production of gold nanoparticles can be achieved through different methods such as chemical reduction, laser ablation, radiolysis and electrochemical methods[iii]. These methods have some drawback, i.e. use of toxic chemicals, expensive and, etc. which posestrong biological and environmental risks[iv]. To overcome such tedious methods and need to replacement of non-ecofriendly synthesis, techniques with non-toxic, environmentally friendly and green chemistry methods is the present need in the preparation of Gold nanoparticles[v].

Now, biological methods have an increasing attention for the synthesis of gold nanoparticles, because biological methods offer clean cost effective and efficient synthetic techniques. Recently, several biological systems such as plant extracts, fungi, bacteria and yeast have been studied[vi]. Plants are capable of reducing metal ions to nanoparticles, wherein plant phytochemicals mediate the less expensive and safest to production of nanoparticles. The green synthesis of AuNPs has been recently reported, where plant extracts such as *Azadirachtaindica*[vii], *Terminaliachebula*[viii], *Cinnamomumcamphora*[ix], Aloe vera[x], Alfalfa[xi] and *Gymnemasylvestre*[xii] have been effectively used for the synthesis of biocompatible, stable and bioactive gold nanoparticles with excellent applications. In the present work, we propose a green synthesis of AuNPs using *Buteamonosperma* gum (BMG) as reducing and stabilizing agent.BMG contains a wide spectrum of components, including Tannins, mucilaginous material, pyrocatechin and polysaccharides[xiii]. BMG is used in ringworm, stomatitis, septic sore throat, excessive perspiration and used for the treatment of leucorrhoea, and diarrhea[xiiii]. Microwave radiation assisted synthesis offers advantages such as operational simplicity, cost effectiveness, rapid reaction times and avoids the traditional harsh treatments like elevatedtemperatures, and lengthy reaction times[xv].In the present investigation AuNPs were synthesized using the gum of BMby microwave irradiation method. The gum solution act as reducing and capping agent and the synthesized gold nanoparticles were characterized for its morphological and structural studies by using UV-Vis, FTIR, XRD and TEM. The green synthesized AuNPs showed exciting catalytic activity for the reduction of Para nitrophenol as a model. And also shows positive antibacterial activity againstklebisellapneumonia and negative antibacterial activity against stayphylococusaureoous,basilusubtilis andEscharesiacoli.This finding could expand our knowledge in the green synthesis of gold nanoparticles and future environmental applications of gold nanoparticles.

MATERIAL AND METHODS

2.1 Materials

$HAuCl_4$ is purchased from Sigma Aldrich India. *Buteamonosperma* gum is collected from the plant located in our University premises. The collected gum is first washed with deionized water to remove dust particles. Then it is oven dried and grind to powder. Allanalytical gradechemicals areused without further purificationin this study. Deionized water is used throughout the experiments.

2.2 Syntheses of gold nanoparticles

In a typical synthesis, 4 mL of 0.5 % gum solution mixed with 2 mL of 1 mM $HAuCl_4$ solution andmicrowave irradiated at 500W for 4 min the reaction mixture. The effect of different parameters such as microwave irradiation time, concentration of gum and concentration of $HAuCl_4$ on nanoparticles synthesis was studied.

2.3 Characterization of AuNPs

Several analytical techniques have been used to investigate the synthesized AuNPs. UV-Vis absorption spectra were recorded by using UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu). The FTIR spectra of the gum and gum capped AuNPs were analyzed by IR Affinity-1(Shimadzu); over a spectral range of 400-4000 cm^{-1}. The X-ray diffraction study was conducted with Rigaku, Miniflex with Cukα radiation. The size and shape of the AuNPs were obtained with TEM (JEOL 2000 FX-II).

2.4 Catalytic reduction of 4-nitrophenol

The typical reaction was carried outin a quartz cuvette,with path length 1cm and 3 mL volume, by mixing 0.3 mL of 2 mM solution of 4-NP with 1 mL of 0.03 M $NaBH_4$ solution and 1.4 mL of water; this leads to the change of color from light yellow to intense yellow.

Immediately 0.3 mL of AuNPs was added to the reaction mixture, the absorption spectra were recorded by UV-Vis spectrophotometer with a time interval of 1 min.

2.5 Antibacterial activity:

Agar well diffusion method:

Agar well diffusion assay was performed according to method [xvi]reported by Tulumoglu,. The target pathogenic bacteria (10^7 CFU/ml) was spread on the Mueller Hilton Agar plates. The agar wells were made using clean and sterile borer and 10,25,50,75,100 µl of sample was added inside the well. Plates were incubated at 37^0 C for 24 hrs. Finally the diameter of the zone of inhibition was measured in (cm). Four pathogen bacteria stayphylococusaureoous, basilussubtilis , klebisella pneumonia, and Escharesiacoli were used in this study.

Results and Discussions

3.1 UV-Vis spectroscopy

UV-Vis spectroscopy is very power full technique to study the kinetics of the formation of AuNPs[xvii]. The UV-Vis spectrum showed the absorption peak at 525 nm was exhibited by the nano metallic gold particles and resulting solution color changes from colorless to red color confirm the successful synthesis of AuNPs. The role of BMG concentration, $HAuCl_4$concentrations and microwave time were studied on the synthesis of AuNPs. Fig 1 shows the effect of BMG concentration on the synthesis AuNPs, studied by microwaving the different concentrations (0.1-0.5%) of BMG containing 2 mM $HAuCl_4$ for 4 min of time. Fig.1a indicates formation of AuNPsand increases with increasing the concentration of BMG. The synthesis was also evaluated by varying the concentration of $HAuCl_4$ (0.1 to 2mM) at constant concentration of BMG (0.5%) for 4 min time (Fig.1b). With the increase the concentration of $HAuCl_4$ the absorption band intensity is increased, which indicates the production of more number of nanoparticles. Absorption spectra of AuNPs prepared at different microwave irradiation times are presented in Fig.1c, whichindicates that the efficiency of AuNPs synthesis increases with the increase in microwave irradiation time.

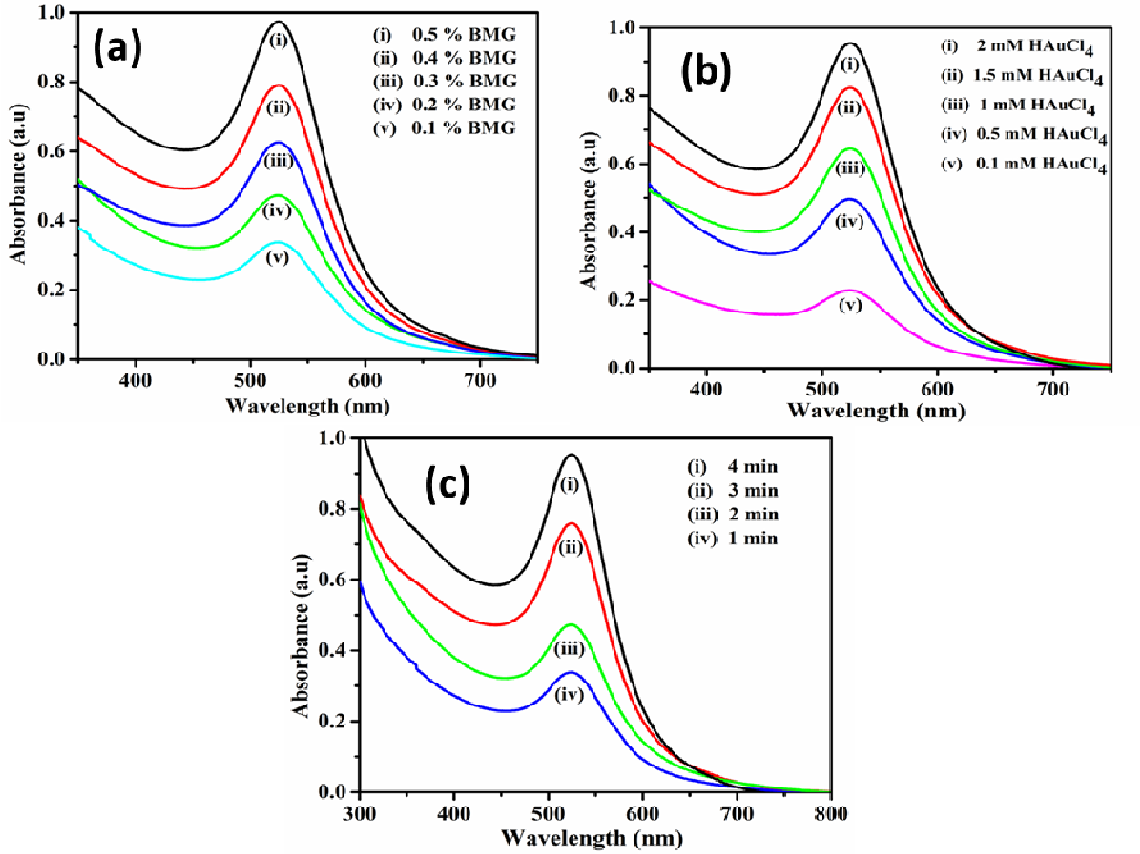

Figure 1.UV visible spectra of AuNPs showing the effect of parameters on the formation of AuNPs: (a) effect of BMG concentration (b) effect of Au^{3+} concentration (c) effect of microwave irradiation time.

FTIR analysis of AuNPs

The FTIR measurements of green synthesized AuNPs and extract were carried out to identify which functional groups are responsible for the reduction and stabilization process. Fig.2 shows the FTIR spectra of BMG and BMG capped AuNPs. FTIR spectra of BMG showed absorption peaks at 3395, 1641, 1515, 1364 and 1219 cm^{-1}. The peak at 3395 may be attributed to-OH stretching vibrations. The peaks 1641 and 1515 cm^{-1} corresponds to asymmetric and symmetric stretches of carboxylate groups. The peak at 1364 and 1219 cm^{-1} assigned to the C-O stretch of carboxylic acids and alcoholic and ether groups. The characteristic absorbance bands of AuNPswere found at 3355, 1746, 1654, 1529, 1368 and 1225 cm^{-1}. A change in the peak positions ofAuNPswere observed with the decrease in band intensity. The absorbance peaks were shifted from 3395 to 3355 cm^{-1}, 1641to 1654 and cm^{-1} 1515 to 1529cm^{-1}, and new peak at 1746 cm^{-1} in AuNPs spectrum indicates the binding of gold ions with carboxylate and hydroxyl groups of the extract[xviii].

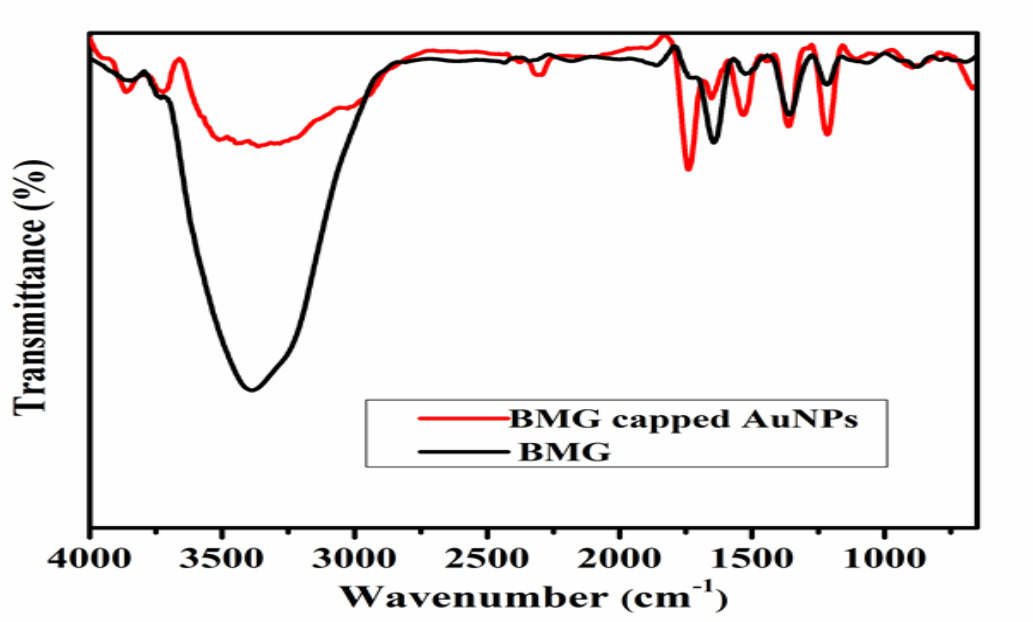

Figure 2. FTIR spectra of BMG and BMG capped AuNPs

3.2 XRD analysis of AuNPs

The XRD pattern of AuNPs was displayed in Fig3. In the XRD spectrum, the Bragg peaks at $2\theta = 38.14^0$ (111), 44.39^0 (200), 64.15^0 (220), and 77.80^0 (311) were observed. These peaks are corresponding to the face centered cubic (fcc) structure of metallic gold. This is in agreement with the standard metallic gold XRD pattern JCPDS no.04-0874. The average crystalline size of AuNPs is calculated from well-known formula Scherrer'sformula[xix].

$D= 0.9\lambda/\beta\cos\theta$

Where D is the crystalline size, β is the full width at half maximum, λ is the wavelength of X-ray used and θ is the Bragg's angle. The average crystalline size was found to be 8 nm.

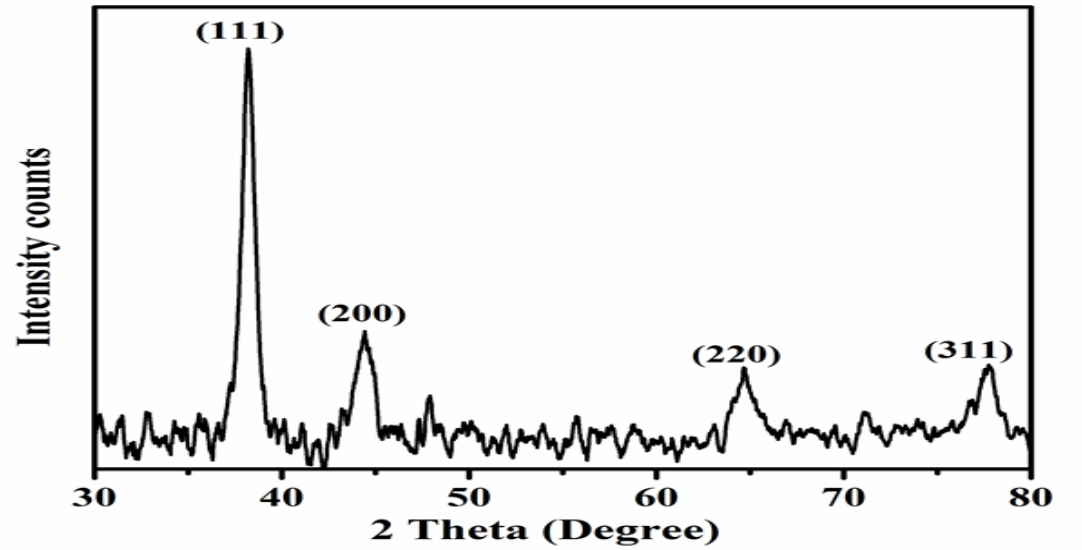

Figure 3. Powder XRD patterns of BMG capped AuNPs

3.3 TEM analysis

The shape and size of prepared AuNPs were studied by TEM. The fig 4a shows that AuNPs synthesized, were mostly monodispersed and spherical shape. The particles are well separated from each other and did not exhibit any aggregation. This indicates the effective capping nature of BMG. The AuNPs size distribution histogram(fig 4b) was constructed and the average size of AuNPs was found to be 12 ± 2 nm.

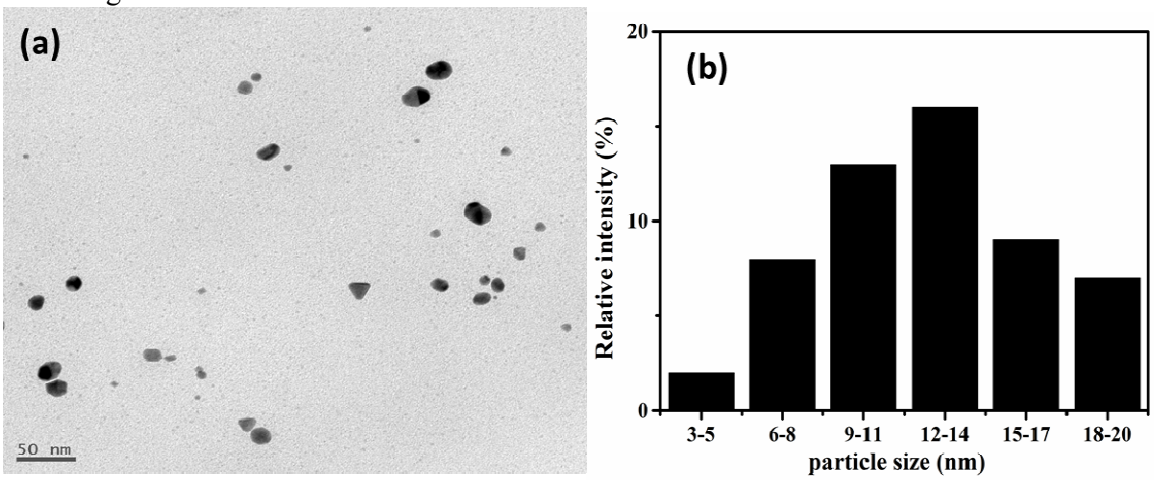

Figure 4 (a) TEM image of AuNPs (b) Corresponding particle size distribution

3.4 Catalytic function of AuNPs

To test the efficacy of AuNPsfor their catalytic activity, the reduction of toxic pollutant 4-NP in the presence of excess $NaBH_4$ is studied. The typical reaction was carried out by taking about 0.3 mL of 2 mM solution of 4-NP, 1 mL of 0.03 M $NaBH_4$ solution and 1.4 mL of water and they were mixed in a quartz cuvette. This reaction was easily monitored by UV-Vis spectroscopy. The absorption peak of 4-NP shows at 317 nm gives peak at 400 nmwith red shift.The addition of $NaBH_4$to the 4-NP the color changed from light yellow to intensive yellow color. This may bedue to the formation of 4-nitrophenolate ion (Fig.5) in the alkaline medium caused by $NaBH_4$. Nochange in peak intensitywas observedon standing the mixture at room temperature for 12 hours. This indicates $NaBH_4$alone cannot reduce 4-NP due to large kinetic barrier for the reduction reaction. The intensity of the absorption peak at 400 nm gradually decreased with time (Fig.6a),finally the peak is disappeared and simultaneously a new peak is appeared at 298 nm with the addition of 0.2 mL of AuNPs to 4-nitrophenolate. The appearance of new peak indicate the formation of 2-aminophenol.

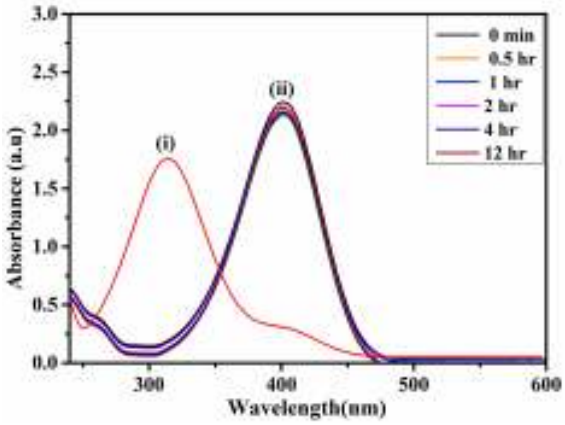

Figure 5 UV–visible absorption spectra of aqueous solutions of (i) pure 4-nitro phenol (ii) 4-nitro phenol in the presence of $NaBH_4$ at different time intervals.

A low intensity peak at 530 nm corresponds to the SPR peak of AuNPS is also observed in the absorption spectra. It is interesting to note that there was no significant shift observed in the SPR of AuNPs throughout reaction process. Even in the presence of a strong reducing agent no agglomeration takes place during the process. This indicates that the AuNPs are stable and catalytic activity of AuNPs was surface reaction phenomenon. The kinetics of reduction is pseudo-first order reaction with respect to 4-NP, as the concentration of $NaBH_4$ was larger than that of 4-NP.Fig 6b shows that there is a good linear relation betweenln (A_t/A_0) and time. Here, A_0 is absorbance at time 0 and A_t for absorbance at any time t. The rate constant (k) was calculated from the slope. The rate constant was found to be 0.032 S^{-1}.

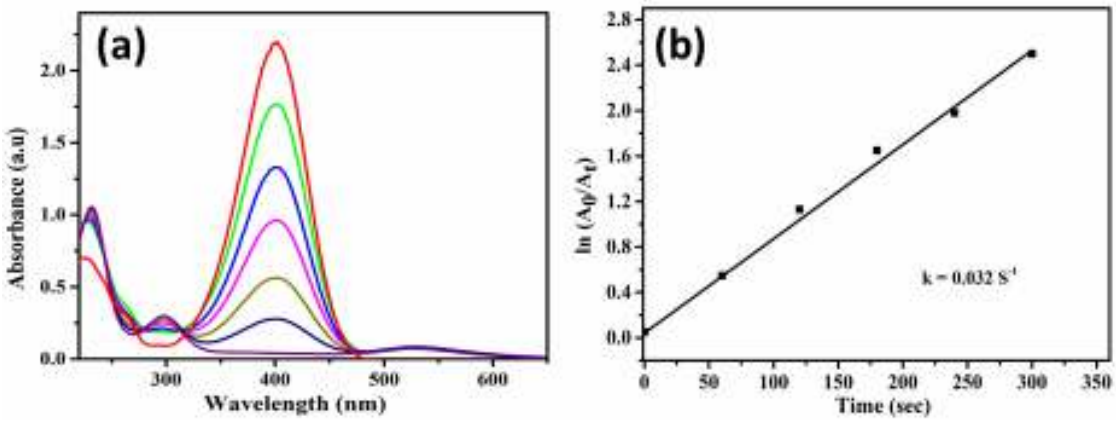

Figure 6 UV (i) absorption spectra of 4-nitrophenolate in the presence of AuNPs (ii) Plot of ln (A_t/A_0) against time for pseudo-first-order reduction kinetic reaction of 4-nitrophenol to4-aminophenol in the presence of excess of $NaBH_4$in aqueous solutions

3.5 Antibacterial activity of gold nanoparticles

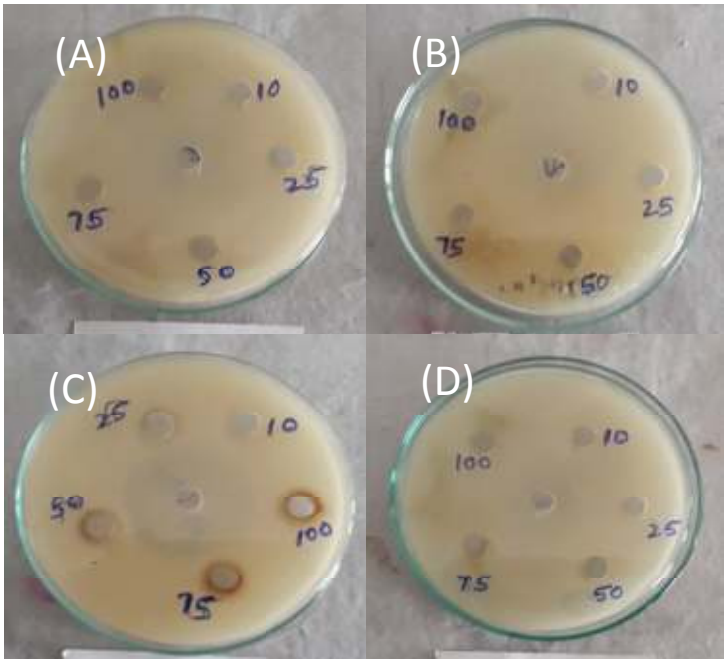

Fig. 7 Antibacterial activity of capped GoldNPs using(a) stayphylococusaureoous(b) basilussubtilis (c) klebisella pneumonia, (e)Escharesiacoli.

Table.1: synthesized AuNPs antibacterial activity.

S No	Stayphylococus aureoous (cm)	Bacillus subtilis(cm)	Klebisella pneumonia (cm)	Escharesia ecoli (cm)
10µl	-	-	0.1(cm)	-
25µl	-	-	0.3(cm)	-
50µl	-	-	0.4(cm)	-
75µl	-	-	0.6(cm)	-
100µl			0.8(cm)	-
50µlExtract	-	-	-	-

Anti bacterial activity zone against selected pathogens

The synthesized AuNPs are showing positive antibacterial activity only against klebisella pneumonia and negative antibacterial activity against staphylococcus, Basillussubtilis and Escharesiacoli bacteria.

Conclusions

In summary, a facile, cost effective, economically viable and green method for the synthesis of AuNPs has been developed by employing gum as both reducing and capping agent. This green synthesis is rapid and produces particles of mainly monodispersed spherical shape with average size of AuNPs is 12±2 nm. The XRD pattern showed that the synthesized AuNPs were crystallinein nature. The catalytic efficiency of AuNPs monitored for reduction of 4-NP by $NaBH_4$ showsa very fast reaction that change the 4-NP to 4-AP with present of AuNPs as catalyst. The synthesized AuNPs were exhibiting positive antibacterial activity against klebisellapneumonia and negative antibacterial activity against stayphylococusaureous,basilussubtilisandEscharesiacoli.The results of this study could be used for further environmental applications.

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