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Facile Green synthesis of Silver nanoparticles using carboxymethyl Neem gum, Evaluation of their Catalytic and Antimicrobial activities

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Abstract : In this work we report simple, ecofriendly, stable silver nanoparticles (AgNPs) were synthesized using carboxymethyl neem gum (CMNG) as both reducing and stabilizing agent. The successful formation of AgNPs was confirmed by UV-Visible spectroscopy (UV-Vis), X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and transmission electronic microscopy (TEM). The XRD studies indicates that the AgNPs were purely crystalline. TEM results showed that the average particle size of the synthesized AgNPs was 12±2 nm. The AgNPs demonstrated the excellent catalytic activity in reduction of 4-Nitrophenol (4-NP) to 4-Aminophenol (4-AP) in the presence of $NaBH_4$.The kinetics of the reaction was found to be of pseudo-first-order with respect to the 4-NP and the rate constant was found0.36 min^{-1}. The synthesized AgNPs showed good antibacterial activity.
Keywords : Green synthesis, Neem gum, Silver nanoparticles, Catalytic activity, antibacterial activity.

1. Introduction

Nanomaterials plays important role in modern science and technology due to their peculiar characteristic properties such as small size (1-100 nm), large surface to volume ratio, biocompatibility, chemical and physical properties, and specialized target binding properties[1,2]. Nanomaterials have been wide-ranging application in various fields such as chemistry, medicine, physics, optics, electrical science and biology. Among several nanomaterial silver nanoparticles (AgNPs) possess some unique chemical and physical characteristic properties like easy synthesis and fabrication, chemical stability, biocidal activity, simple and easy to functionalization[3-5].

Generally, the silver nanoparticles are synthesized and stabilized through physical, mechanical and chemical methods, photochemical reactions and electrochemical techniques[6,7]. These methods are expensive, time taking and require the use of toxic chemicals as reducing and stabilizing agents to overcome drawbacks of these methods researchers introduced green chemistry method. Green synthesis of AgNPs is an attractive method due to it is eco-friendliness, simplicity and biocompatibility. Several biological systems such as plant extracts, fungi, algae and bacteria can easily reduce Ag^{+1} to form silver nanoparticles in an ecofriendly manner[8-11].

Here we report Carboxymethyl neem gum reduced and stabilized AgNPs. Neem gum is obtained from the tree of *Azadirachta indica* (family: Meliaceae) and a naturally available polysaccharide compound. The

main polysaccharide chain consists of arabinose, glucose, fucose, mannose, xylose, glucosamine and galactose. Neem gum is used as a laxative, in cosmetics, food industries and in drug delivery[12,13]. Chemical modification of natural gums has been employed to improve their properties as biopolymer. Carboxy methylation is one of the several strategies used for the functionalization of natural polymers. It is widely used modification method because of its lower cost of chemicals and ease of processing. Carboxymethyl derivatives are generally polyelectrolyte with enhanced aqueous solubility and are used in drug delivery applications, etc. During previous studies, this method has been employed to synthesize high performance macromolecule materials[14].

Nitrophenols are widely used in many industries such as textiles, chemical labs, cosmetics, ceramic and companies manufacturing explosives. This release of these toxic, carcinogenic pollutants and chemically stable in wastewaters. The traditional wastewater treatment methods, including chemical coagulation and adsorption these techniques cannot be effective and sufficient in the reduction of these compounds to non-dangerous product because of their high stability, high resistance[15]. Therefore, scientists have mainly focused on the reduction of these compounds.

In the present study, we investigate the synthesis of silver nanoparticles using CMNG as a reducing and stabilizing agent. These CMNG mediated AgNPs was characterized by UV-Vis spectroscopy, FTIR, XRD and TEM. To the best of our knowledge this is the first time to use CMNG in synthesis of AgNPs. The AgNPs were tested their catalytic activity against for the reduction of 4-NP and antibacterial activity were tested against gram negative and gram positive bacteria.

2. Experimental

2.1 Materials

The starting material for the synthesis of AgNPs was Neem gum, obtained from the Girijan Co-operative Corporation Limited, Hyderabad. All the reagents used were of analytical grade and used without further purification. The solution of above chemicals was prepared in double distilled water.

2.2 synthesis of CMGK

Carboxymethylation of neem gum (NG) was carried out employing monochloroacetic acid. NG (1g) was dispersed in 80 ml of ice cold NaOH solution (45%, w/w) with stirring for 40 min, followed by the addition of 10 ml of monochloroacetic acid solution (75%, w/v) under constant stirring. The reaction mixture was then heated to 75 ºC under constant stirring for 40 min, cooled and suspended in 80 % (v/v) methanol. The precipitate so obtained was then filtered and washed with glacial acetic acid till washing were neutral. The product so obtained, was washed three times with 60 ml portions of 80 % (v/v) methanol filtered and dried in hot air oven at 40 ºC[16].

2.3 synthesis of silver nanoparticles using CMNG

In order to synthesize CMNG capped silver nanoparticles, 1 ml of $AgNO_3$ and 3 ml of CMNG solution were taken in a boiling tube and boiling tube was sealed with aluminium foil. The reaction mixture was kept in an autoclave at 121 ºC and 15 psi pressure for different durations of time. The resulting yellow color of the

solution indicates the formation of silver nanoparticle

2.4 Catalytic reduction of 4-NP

To check the catalytic activity of AgNPs reduction of 4-NP taken a model reaction. In a typical experiment, an aqueous of 1.8 ml of 4-NP (0.25 mM) was mixed with 1 ml of $NaBH_4$ (0.16 M), these reaction mixture was taken in a quartz cuvette. 0.5 ml of AgNPs was added to the above mixture and monitored by recording the UV-Vis spectra at 1 min time intervals.

2.5 Characterization

The green synthesized were analyzed by UV-Visible spectrophotometer (UV-3600, Shimadzu).The FTIR analysis was carried out the synthesized AgNPs with the help of FTIR Spectrophotometer (IRAffinity-1,

shimadzu) in the scanning range of 650-4000 cm^{-1}. The crystallinity of the AgNPs was studied by XRD (Rigaku, miniflex). TEM analysis was performed using a transmission electron microscope (JEOL 2000 FX-II)

3. Characterization of AgNPs

3.1. UV-Vis spectra

The silver nanoparticles formation was primarily observed by UV-Vis spectroscopy. A distinct yellow color was observed due to the phenomenon of surface plasmon resonance (SPR) band, which is dominated in the UV-Vis spectra are according to the shape, size and interaction with the medium. In UV-Vis region AgNPs exhibited sharp absorption peak at 415 nm due to its SPR. Figure 1 shows effect CMNG concentration on the synthesis of AgNPs was studied by autoclaving different concentration of (**0.1-1 %**) of CMNG solution containing 2mM of AgNO3 for 20 min. From Figure 1 it's suggested that with an increasing in CMNG concentration there is an increasing in absorbance intensity it indicates that formation of AgNPs increases[15].

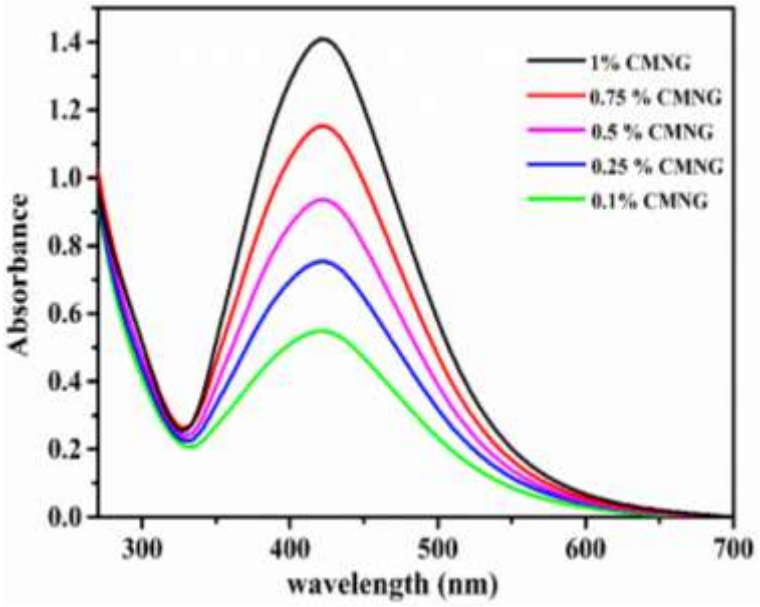

Figure 1. The UV-vis absorption spectra of silver nanoparticles synthesized different concentrations of CMNG

The synthesis of AgNPs was also studied by varying the concentration of $AgNO_3$ and CMNG was constant concentration (**1%**). It reveals that the amount of AgNPs synthesized, increases with the increases in concentration of $AgNO_3$ shown in Figure 2.

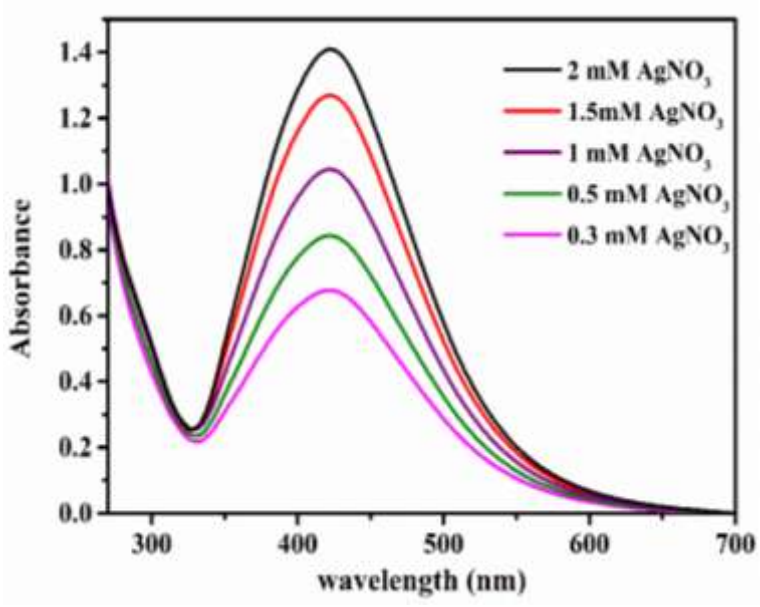

Figure 2. The UV-vis absorption spectra of silver nanoparticles synthesizeddifferent concentrations of $AgNO_3$

3.2 FTIR

The fabrication of AgNPs was tracked by FTIR spectroscopy. Figure 3 curve (a) and curve (b) shows the FTIR spectra of CMNG and CMNG capped AgNPs respectively. The major peaks are found in the FTIR spectrum of CMNG are 3479, 2882, 2125, 1649, 1421, 1371, 1242 and 1082 cm^{-1}. The broad peak at 3479 cm^{-1} could be suggest the -OH groups, at 2882 asymmetric stretching of methylene group, peak at 1649 cm^{-1} could be suggest an asymmetric stretch of carboxylate groups. The peaks at 1421 and 1242 cm^{-1} could assign to bending of -C-H and C-O stretching vibrations of polyols respectively. FTIR spectra of CMNG capped AgNPs showed peaks at 3424, 2887, 2123, 1636, 1544, 1384 and 1057 cm^{-1} respectively. FTIR spectrum of CMNG capped AgNPs, a shift in the absorbance peaks was observed from 3479 to 3424, 1649–1636 and 1421–1544 cm^{-1}. The FTIR analysis suggests that the hydroxyl and carbonyl groups have responsible for the reduction and stabilization of AgNPs.

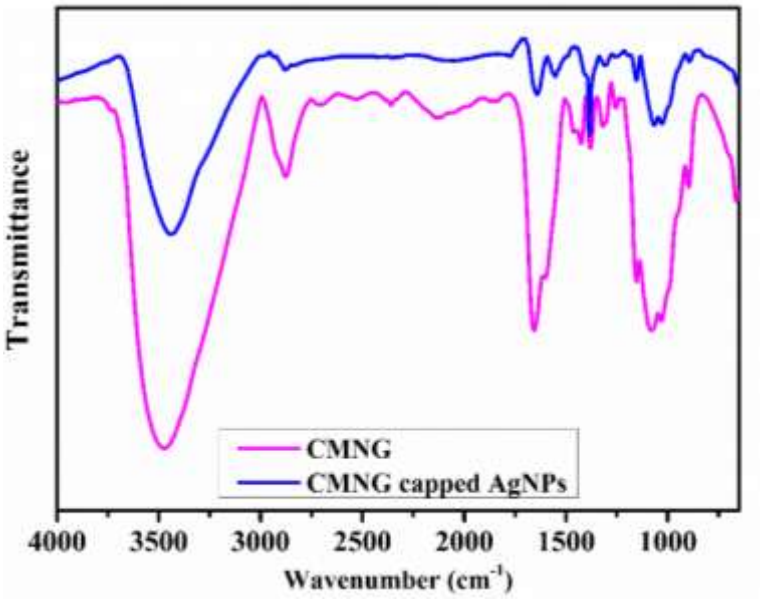

Figure 3. FTIR spectra of CMNG and CMNG capped gold nanoparticles.

3.3 XRD

The XRD analysis was performed further confirmation of nanosized AgNPs synthesis. The AgNPs(Figure 4)show clear peaks at 2θ 36.98 (111), 44.16 (200), 64.14 (220), 76.42 (311), these values are closely related to the reported standard XRD pattern of Ag (JCPDS file no.04-0784) and previous reports suggesting crystalline FCC (face centred cubic)structure of synthesized AgNPs. Crystalline size of AgNPs was calculated using the Scherer's formula from the XRD pattern and was found to be around 9.2 nm. The observed from XRD analysis are in good agreement with the TEM analysis.

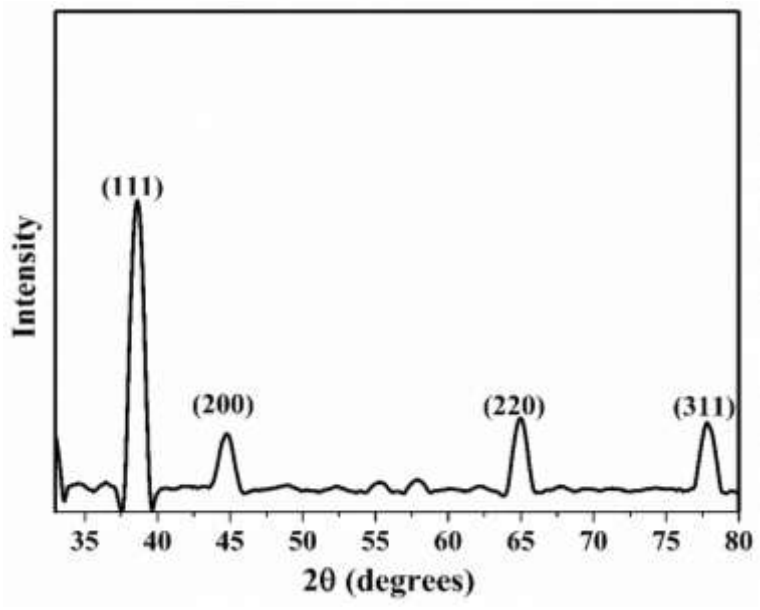

Figure 4.X-ray diffraction pattern of synthesized AgNPs.

3.4 TEM

The shape and size of AgNPs were observed with the help of Transition Electronic Microscope. TEM (Figure 5) analysis revealed that the plant extract mediated synthesized AgNPs are mostly spherical along with few irregular shapes. Histogram (Figure 6) constructed by considering 120 nanoparticles indicates that the average particle size distribution is 12±2 nm.

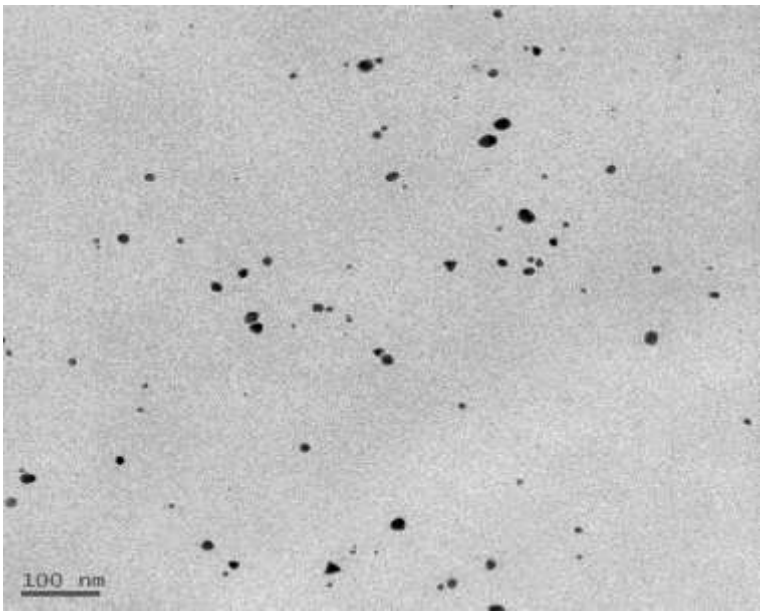

Figure 5. TEM images of CMGK capped AgNPs

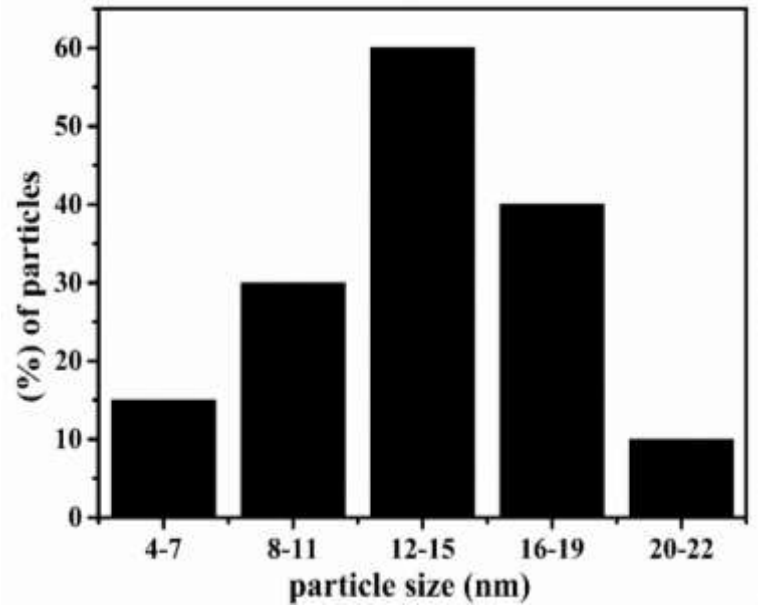

Figure 6 Histogram showing the particle size distribution of AgNPs.

3.5 Catalytic reduction of 4-NP

In present days, the catalytic reduction of 4-NP in the presence of excess $NaBH_4$ have been as the evaluation method for studying the catalytic activity of various metal nanoparticles (ref). Here, to investigate the catalytic ability of the as synthesized AgNPs, an appropriate amount of AgNPs were added into the reaction system containing 4-NP and $NaBH_4$. The reaction was started after mixing 1.8 mL of 0.25 mM 4-NP with 1 mL of 16mM $NaBH_4$ in a quartz cuvette leading to the change of color from light yellow to intense yellow. Figure 7 shows the absorbance peak at 318 nm is assigned to pure 4-NP. The peak shifts to 401 nm after addition of $NaBH_4$ which is due to the formation of p-nitrophenolate ion. The reaction of 4-NP to 4-AP using aqueous $NaBH_4$ is thermodynamically favourable (E^o for 4-NP/4-AP =-0.76 V and H_3BO_3/BH^-_4 = -1.33 V versus NHE). The presence of kinetic barrier due to the large potential difference between donor and acceptor molecules decreases the feasibility of this reaction[15]. Figure 7 shows there was no change of the peak at 400 nm, it indicates that $NaBH_4$ itself was not able to reduce 4-NP directly without addition of AgNPs.

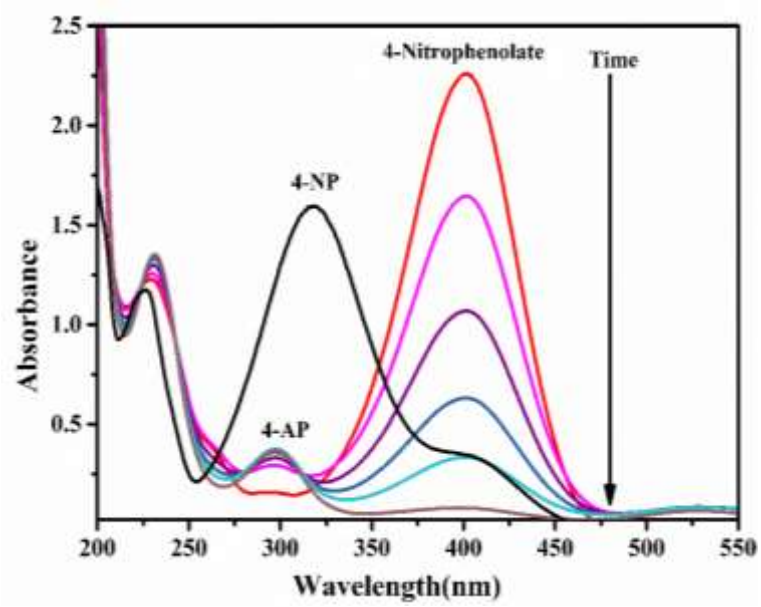

Figure 7.UV–Visible spectra recorded during the reduction of 4-NPwith $NaBH_4$catalyzed by AgNPs

Figure 7 shows the UV-Vis absorption spectra of the 4-NP-$NaBH_4$ system in the presence of 0.5 mL of synthesized AgNPs at different time durations. With the increase in reaction time, the peak at 401 nm is gradually decreased and simultaneously, a new peak at 299 nm appeared, which can be attributed to the reduction of 4-NP and formation of 4-AP[15]. After 5 min the peak at 401 nm related to 4-NP almost disappeared, indicating that the reduction of 4-NP was closely completed. These results show that the as-obtained AgNPs has a good catalytic capacity for the reduction of 4-NP to 4-AP.

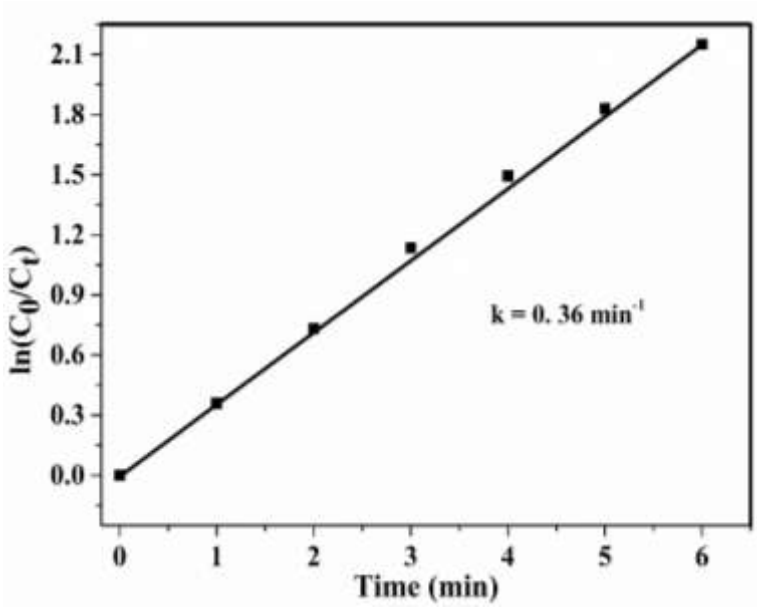

Figure 8.The plot of ln (C_0/C_t) versus time for the reduction of nitrophenol to aminophenol

The rate constant of the reduction reaction is of pseudo first order with respect to 4-NP, concentration of $NaBH_4$ greatly exceeds that of 4-NP and the reduction reaction rate can be assumed to be independent of $NaBH_4$ concentration. The rate constant (k) was calculated from the linear plot of ln (C_0/C_t) (where C_0 is the absorbance at the initial time, C_t the absorbance at the specific time) and reduction time in minutes (Figure 8). The rate constant is calculated from the slope of this graph and is found to be 0.36 min^{-1}.

3.6 Antibacterial activity

The antibacterial activity of green synthesized silver nanoparticles was studied against *E-coli* a gram negative and *B. subtilis* a gram positive bacteria. The antimicrobial efficiency of AgNPs increases because of their larger total surface area per unit volume[15]. The diameter of inhibition values for the both samples was recorded. The zone of inhibition of E-coli and B. subtilis were observed around the disc, as shown in Figure9 it can indicate that no zone of inhibition was observed for the CMNG alone and AgNPs effective bacterial activity in E-coli than in B. subtilis. The present results agree well with the work of earlier reports[17]. It can however be concluded that the green synthesized AgNPs showed effective antibacterial activity on both the gram classes of bacteria.

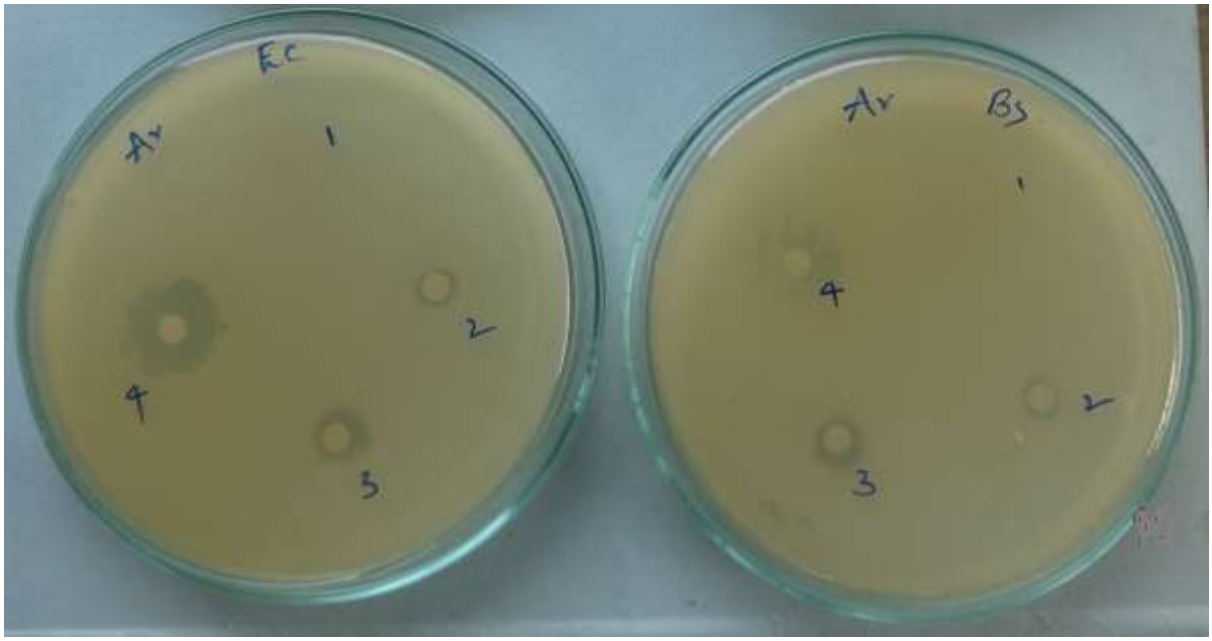

Figure.9. Antibacterial activity of AgNPs against B. subtilis and E. coliafter 24 h of incubation.

Conclusion

In summary, a navel, cost-effective and green synthesis of AgNPs was developed through the reduction of the aqueous $AgNO_3$ solution using CMNG as reduction and capping agent. The synthesized AgNPs were characterized by XRD which conform the FCC structure, TEM results revealed that the size of the nanoparticles was around 12±2 nm. The hydroxyl and carbonyl functional groups present in the CMNG were found to be responsible for the formation and stabilization of AgNPs. Our results also demonstrated that the AgNPs can be used as an excellent catalyst for the reduction of 4-NP in $NaBH_4$ solution. Particularly the rate constant was 0.36 min^{-1} for the reduction of 4-NP to-AP. The novel catalyst is anticipated to have extensive practical applications in the field of organic catalysis.

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