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The calorimetric detection and anti-oxidant activity of green synthesized silver nanoparticles

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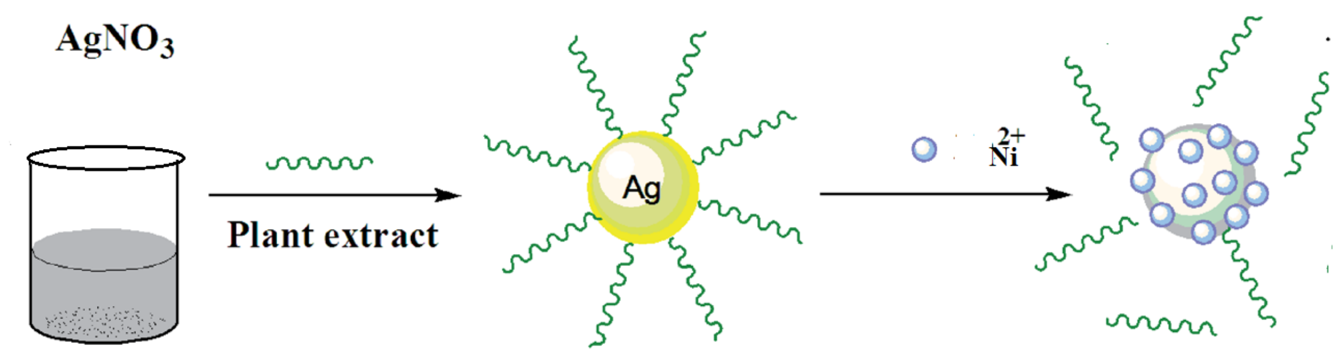
Novelty and Highlights

1 – AgNPs were synthesised by an eco-friendly and simple method from plant extract

2 – The calorimetric sensor used for the selective detection of metal

3 – Both the plant extract and synthesized AgNPs were used for investigation of Anti-oxidant Activity

Graphical Abstract



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The calorimetric detection and anti-oxidant activity of green synthesized silver nanoparticles

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Abstract: This report describe a simple, sensitive, a work of literature and economical approach for the green synthesis of silver nanoparticles by using green fruit methanolic extract of *Dalbergia sisso*. AgNPs were synthesised at room temperature which showed an intense peak at 412 nm, confirmed by UV-Vis spectrometer and with a yellow colour formation. The pH concentration and time study for synthesis are investigated. For calorimetric interference, there was a difference in spectral peaks for corresponding plant extract, AgNPs and Ni2+ containing AgNPs. The plant extract and AgNPs had excellent anti-oxidant activity, but AgNPs showed more free radicals scavenging ability then the plant extract.

Keywords*: Silver Nanoparticles, Calorimetric, Anti-Oxidant.*

Introduction

Nanotechnology is very important and advances field because many industries use this technology for human comforts so it has a great impact on our life [1]. Nanoparticles have distinctive properties as a consequence of their size, distribution and morphology and, hence, are an extremely significant constituent in the rapidly developing field of nanotechnology [2] because of its importance [3]. those particles whose diameter is less than 100nm are more dynamic and also the weight of nanoparticles have a greater surface area as compared to larger particles so this higher surface area of nanoparticles makes them reactive and they can react more as they become explosive and absorbs faster as compared to larger particles[4,5,6]. The nanoparticle has many properties due to its advance in nature so there is also variation in nanoparticles such as a silver nanoparticle, gold nanoparticles etc [7-10]. Natural method or biological method of manufacture of nanoparticles are called ‘’Greener synthesis of nanoparticles which have no harmful effect on human life but it is slow in action and it performs its good activity which is used for many research purposes for better production of nanoparticles which has many applications [11].bacteria and fungi [12] enzymes[13]. Silver based compounds are much cheaper easier than gold based one; moreover, silver nanoparticles are now considered as an important class of nanomaterials. They are presently mainly used as a catalyst and they are widely used in research methodology [14, 15]. Nanomaterials are also used in higher industries and in many technologies and in solar energy in our daily life sciences in the purification of water or making the water drinkable by removing the metals [16, 17]. The three main concepts for the preparation of nanoparticles in a green synthesis approach are the choice of the solvent medium (preferably water), an environmentally friendly reducing agent, and a non-toxic material for the stabilization of the nanoparticles [18, 19]. To be energy capable, the synthesis processes should be carried out close to ambient temperature and pressure and under neutral pH. [20]. Nanoparticles have unique properties as a significance of their size, distribution and morphology and, therefore, are a very important factor in the fast increasing field of nanotechnology. [21]. In the majority of cases, silver participates in its nitrate form, thus suggesting a strong antimicrobial effect but when silver nanoparticles.

Experimental

Material and chemicals: The plant green fruits were collected from the different area of Bannu, KP- Pakistan. All chemicals used in this work were of the high pure analytical grade. Silver nitrate ($AgNO_3$, 99.8%) was purchased from Sigma Aldrich (Germany). The stock solutions of each metal ion were prepared by dissolving a known amount in deionized water. All the glassware was thoroughly washed with aqua regia and then with deionized water.

Extract Preparation: Fruits were grinded properly in a blender. The grinded mixture was soaked in 1000mL methanol in a conical flask and covered it. Put it in a shaker for about 12 hours. After shaking the mixture was filtered. This solution placed in open air for the purpose of methanol evaporation. The methanol was evaporated and the pure dry extract left in the bottom of the container. The crude extract of plant got prepared.

Synthesis of Silver nanoparticles: The $AgNO_3$ solution of 0.01M concentration was diluted up to 10mL with deionized water (0.001M). in a conical flask and adjust the pH by NaOH of 0.01M. 1mL extract solution added to this mixture. Its spectrum peak was taken at about 412 nm by UV-Visible Spectrophotometer.

Colourimetric detection of Mn^{2+}: The stabilized green synthesized AgNPs were used for Ni^{2+} colourimetric detection. A series of solutions were prepared. After adding Ni^{2+} to diluted AgNPs solution. The colour change was confirmed by absorption spectra recorded by double beam UV- Vis spectrophotometer. The colour change can also be detected by naked eye. It was shown that the increase in concentration resulted in a gradual decrease in absorbance.

Antioxidant Activity: 0.001g of DPPH per 50mL methanol and 0.03g extract per30mL methanol solution were prepared and same for Ascorbic acid. Take 25, 50, 75 and 100 µL/mL Ascorbic Acid solutions and dissolve in 975, 950, 925 and 900 µL/mL DPPH solution and shake them well. Keep it for 15 to 20 minutes for incubation. Now note its absorbance at 517nm by UV-Vis Spectrophotometer. Same for Plant extract and AgNps were also done. To determine that how much free radical was scavenged the following equation was used. DPPH Scavenged (%) = (Abs of DPPH−Abs of Antioxidant)/(Abs of DPPH) ×100.

Results and discussion,

Effect of pH: The five solutions were prepared. Their p^H was adjusting by adding NaOH to 10 mL diluted solution of $Ag(NO)_3$ at 7, 8, 9, 10, 11 and 12 respectively. In plant extract solution different organic compounds are present like phenols, amines, triterpenoides, protein and fibres. These compounds contain OH groups.

The OH groups of NaOH interact with $AgNO_3$ and form AgOH which is basic in nature. By the addition of NaOH to $AgNO_3$ the p^H of the solution increases and become basic in nature. After adding 1mL extract of *Dalbergia sisso* to each of the solution the change in colours of solutions was observed. After about an hour the colour of solutions will appear dark brownish he spectra of all the samples were taken by double beam UV spectrophotometer. All samples show very good absorption and the given very intense spectra. But the sample having p^H 9 given the maximum absorption and shows the most intense peak. While the peaks at p^H 7, 8, 10, 11 and 12 are below the peak of p^H 9. It means that the p^H 9is the best suitable p^H for synthesis of AgNPs from the extract of *Dalbergia sisso* green fruits.

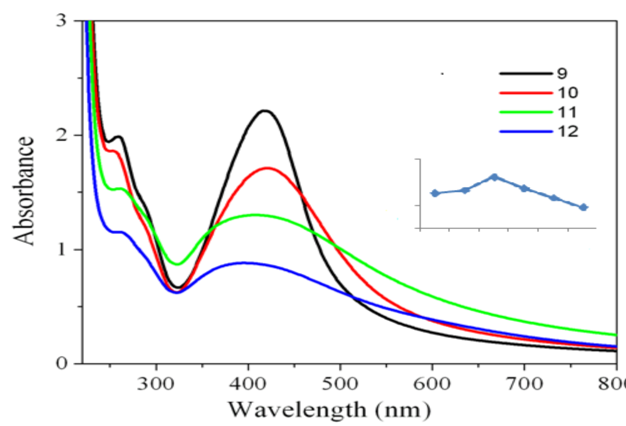


Fig 1. Represent the pH effect on the synthesis of AgNPs

Time Study: To check that after how many the AgNPs which was synthesized by using extract get stable, the time study was performed. For this purpose NaOH added to 0.001M (0.1mM) solution of $AgNO_3$ and adjust its p^H on 9 add 1mL extract solution to it. As the AgNps were synthesized the colour changed was immediately noted and check its absorbance at 0 min by UV Vis spectrophotometer, after that the absorbance was check at different time interval like 1hour, 18hours and 20hours respectively. There was regular increase in the synthesis of AgNPs from 1hour to 20 hours.

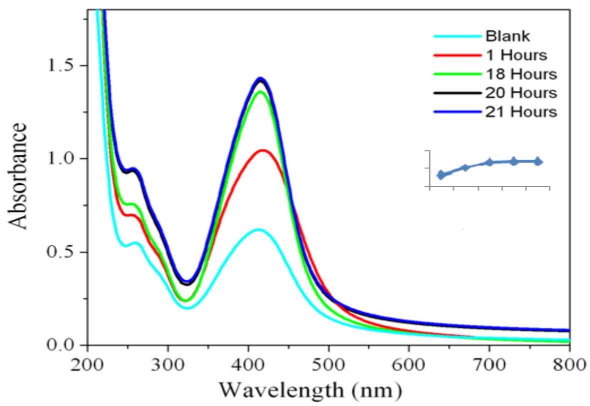


Fig 2. show the synthesis of AgNPs at different time intervals

After that the AgNPs get stable and there was no further increase in the absorbance. And after 20 hours there will be no change in its peak as it shows stability.

Concentration study of Plant extract: The AgNPs was synthesized by using plant extract so to determine that at which concentration there is more synthesis. Six solutions were prepared by adding NaOH to 1×10 $^{-3}$ M $AgNO_3$ and adjust its p^H at 9. Now different concentrations of 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL, 1.0 mL of extract solution added to them. The solutions start to change the colour to dark yellow which indicates AgNPs synthesis. The absorbance was noted by using UV Vis spectrophotometer. The absorbance increase as the concentration increases and maximum absorbance noted at a concentration of 1.0 mL. This indicating that at 1.0 mL concentration there is more AgNPs formation and by increasing there will no more AgNPs synthesis because all the Ag^{+1} reduced and there is a decrease in SPR intensity and decrease in absorption spectrum occurred.

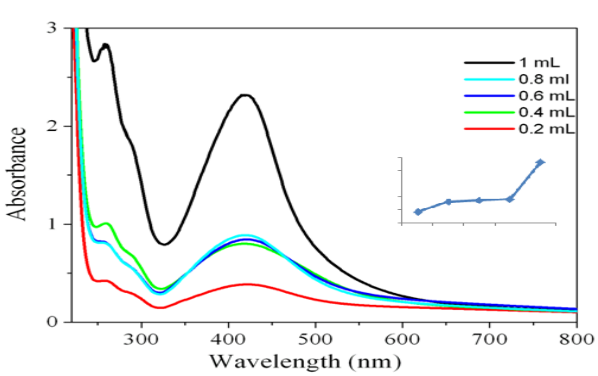
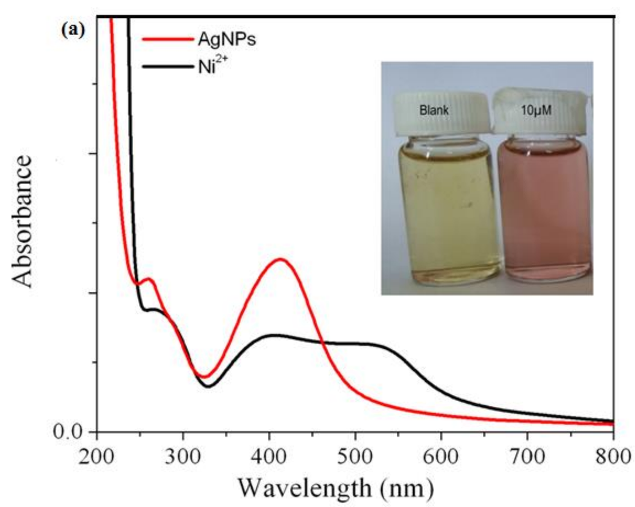


Fig 3. Effect of plant extract on the synthesis of AgNPs

Colourimetric detection of Ni^{2+}: The silver nanoparticles were prepared by using plant extract and its colour was appeared yellowish-brown, This occurs because of a phenomenon which is called SPR. It is the abbreviation of Surface Plasmon Resonance. It takes place in metallic nanoparticles like silver, which showing diverse colours. Its happened due to the presence of free electrons in AgNPs. The moving light frequency resonates with them which cause to appear SPR bend in the area of infrared and visible. When 1×10^{-2} M of Ni^{+2} added to 10mL diluted solution of green synthesised AgNPs , then its colour change from yellow to grey and due to which its SPR bend intensity decrease as shown in Fig: along with photographic image of its corresponding colour change, this change of colour reveal that the colorimetric detection of Ni^{2+} can be performed with green synthesised AgNPs. The AgNPs is a strong sensor because Ni^{2+} is strongly bound with the surface of AgNPs and moving the plant stabilizing agent from the surface of AgNPs, It causes to slight red shift of SPR peak. Furthermore different concentrations of Ni^{2+} added to AgNPs as 25 µM, 50 µM, 75 µM, 100 µM, 150 µM, 200 µM. There was regular darkness of red colour of Ni^{2+} containing AgNPs. After the completion of reaction time about an hour, the spectra were taken by spectrophotometer. There was a continuous decrease of SPR band by increasing concentration of Ni^{2+}. The reaction time was about an hour because Ni^{2+} immediately moves to the surface of AgnNPs.



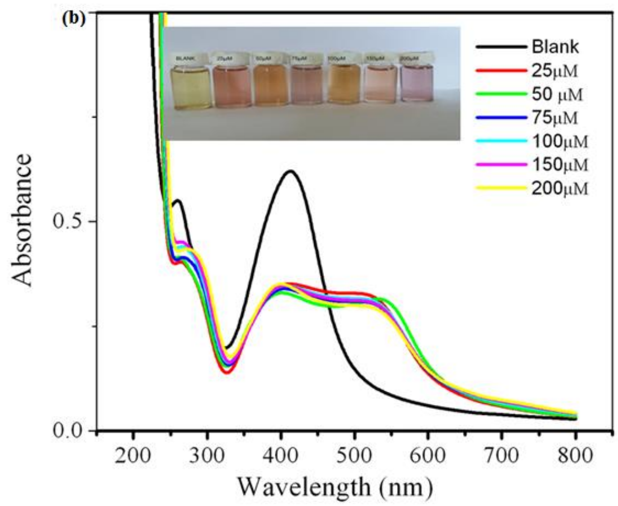


Fig 4. The calorimetric study of AgNPs that corresponding (a) Metallic Interference and (b) Calorimetric detection study of Ni^{2+} with different concentration

Ant-Oxidant Activity: The silver nanoparticles and plant extract have a fantastic antioxidant activity. They have the ability to scavenge free radicals present in the solution like the solution of DPPH. DPPH is an organic compound of dark colour crystalline powder which contains stable free radical molecules. The AgNPs remove these free radicals and show their antioxidant activity. AgNPs. Both have good scavenging ability; however, AgNPs scavenge more free radical then plant extract as shown in fig 5.

AgNPs were synthesised by an eco-friendly and simple method using *Dalbergia sisso* green fruit extract at room temperature. The extract has been used as a reducing agent for the formation of silver nitrate into silver nanoparticles. AgNPs of *Dalbergia sissoo* showed a higher anti-oxidant activity compared to *Dalbergia sisso* green fruit extract alone or silver nitrate. The prepared AgNPs were highly sensitive to Ni^{2+} ions. These colourimetric sensors could be used in both quantitative and qualitative detection of metal ions such as Ni^{2+} ions with the detection limit if different molar concentration and also could be easily visualized with the naked eye or by using UV-Vis spectrophotometer.

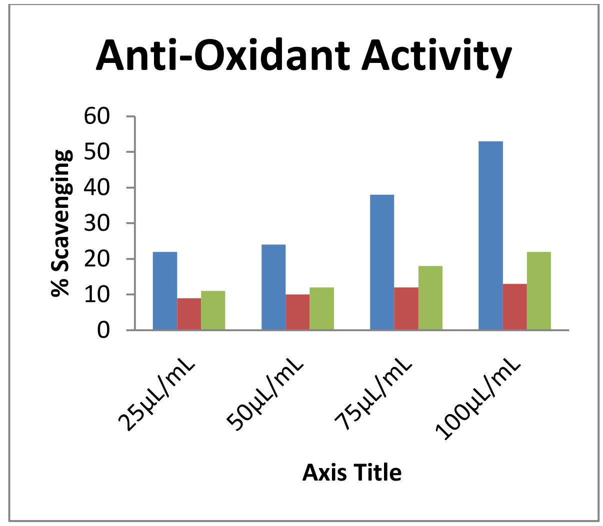


Fig 5. Represent the Anti-Oxidant Activity where blue colour show the percent scavenging activity of Ascorbic acid, red plant extract and green AgNPs scavenging ability**.**

Conclusion

AgNPs were synthesised by an eco-friendly and simple method using *Dalbergia sissoo* green fruit extract at room temperature. The extract has been used as a reducing agent for the formation of silver nitrate into silver nanoparticles. In most of the green synthesis of AgNPs leave extract has been used, but the abilities of other plant parts such as green fruit as capping and reducing agent is not tasted and well defined. In the present work we found that fruits can also be best source for synthesis of AgNPs. These colorimetric sensors could be used in both quantitative and qualitative detection of metal ions such as Ni^{2+} ions with the detection limit if different molar concentration. Plant-AgNPs of *Dalbergia sissoo* showed a higher anti-oxidant activity compared to Dalbergia sisso green fruit extract alone or silver nitrate.

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