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Synthesis, Characterization, Catalytic Activity and Metal Sensing Performance of Silver Nanoparticles.

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Key Words: *AgNPs, Sodium borohydride, diazobenzene, Metal sensing performance*

ABSTRACT

In the present study, the chemical synthesis of silver nanoparticles is carried out using sodium borohydride as a reducing and capping agent. The produced Ag NPs are characterized for their surface morphology and elemental composition. The XRD, FESEM, EDX, FTIR and UV-VIS analysis confirmed the presence of crystalline spherical shaped agglomerated Ag NPs. The Ag NPs are found to be more effective material for catalytic activity in organic synthesis and the heavy metal sensing performance.

INTRODUCTION

Nanotechnology is the technology of material dealing with very small dimensional material usually in the range of the 1 to 100 nm. It is the engineering of designing, characterization, production and application of structure and device by controlling their size and shape in nanoscale. Nanoparticles are synthesized by various methods like Physical, Chemical, Biological and hybrid methods. Many chemical methods have been reported to synthesize silver nanoparticles from silver salts. The fundamental chemical method is the reduction of metal ions in aqueous solution [1]. Due to the importance of homogenous nanometer-sized particles in terms of both technology and fundamental science, they have been actively developed [2]. As the shape and particle size distribution are highly dependent on the type of reducing agent used, the selection of appropriate reducing agent is also an essential factor.

Chemical reduction using organic and inorganic reducing agents is the most versatile and economical method for the synthesis of silver nanoparticles. It is easy to control the shape and size of metal nanoparticles. Silver ions (Ag^{+}) can be reduced in aqueous or non-aqueous solutions with a variety of reducing agents, including sodium borohydride, sodium citrate, ascorbate, N-N dimethylformamide (DMF). The reduction of Ag+ by these reducing agents results in the formation of metallic silver (Ag^{o}), which are then aggregates into oligomer clusters. Metallic colloidal silver particles are eventually produced by these clusters [3]

Nanoparticles have many applications in areas such as optics, chemical industries, drug-delivery, energy science, sensors, agriculture, food packaging and processing, energy science, catalysis, light emitters, biomedical science and also in organic synthesis. It is used as catalyst in several chemical reactions. The residual energy and high

surface-to-volume ratio of metal nanoparticles are primarily responsible for their catalytic activity in a wide range of organic transformations. Between the homogenous and heterogeneous catalysis, nanosized catalysts can acts as a bridge [4, 5]. Though the heavy metals are essential for human survival, an excess quantity of them can cause more health problems such as blood cell raptures, kidney failure and nausea. For detection of heavy metals several analytical methods like AAS [6], ICP-OES [7], and ICP-MS [8] are reported but these techniques require more sophisticated instrumentation and complicated sample treatment.[9-11] Therefore, one can adopt a simple, inexpensive and reliable one step detection approach which can sense the presence of heavy metals.[12]

In the present study chemical synthesis of silver nanoparticles was carried out using the sodium borohydride as a reducing as well as capping agent. Thus synthesized silver nanoparticles are characterized by several techniques to find their shape, size and composition. Afterwards, their catalytic activity in organic synthesis and the heavy metal sensing performance was reported.

Materials and Method

Materials

Silver nitrate (99% pure) and Sodium borohydride (99% pure) were purchased from Alpha Aesar Chemicals and used further without purification. The sodium borohydride used as a reducing agent as well as stabilizing agent. A stock solution of silver nitrate 0.01M was prepared by dissolving 0.0169g/100 ml conductivity water.

Synthesis Method

For both the formation of the ionic silver and the stabilization of the silver nanoparticles, a significant excess of sodium borohydride is required[13]. The 30 ml of 0.01 M sodium borohydride was added dropwise to 10 ml of 0.01 M silver nitrate solution with an arrangement that had been chilled in an ice cold bath with vigorous stirring. When all the sodium borohydride was added, the solution turned a grey, then extra 2 ml of sodium borohydride was added. The entire addition took about 3-4 minutes. To stabilize the particles, the solution was left in the dark for 1-2 days. After that decant the supernatant solution, collect the particles in a china dish and dry them for 1-2 hours at 60° C in hot air oven. Grey coloured silver nanoparticles were formed.

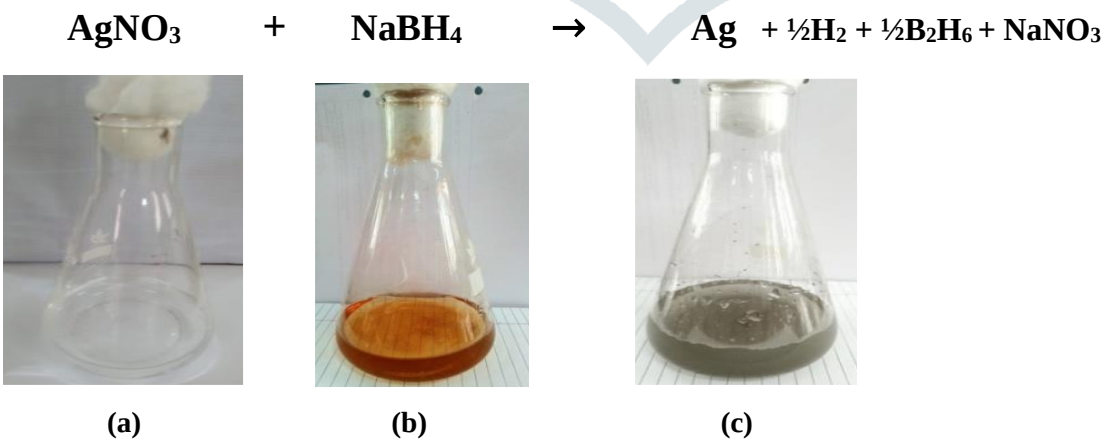

Fig.1: (a) Precursor solution of AgNO3, (b) Change in colour after addition of reducing agent, (c) Change in colour after complete addition of reducing agent.

CHARACTERIZATION TECHNIQUES

The characterization of material is a process by which material structure and properties are probed and measured. In the present study the XRD analysis was carried out using X-ray Diffractometer (powder method) Pan analytical XPert Pro system with CuKα1(1.540Å) radiation, UV-VIS spectroscopy was used to record the spectra of AgNPs with Shimadzu UV-1800 spectrophotometer. FTIR Analysis were obtained by Shimadzu IR-Affinity (Diamond ATR) FT-IR spectrometer in the diffuse reflection mode. The surface morphology of AgNPs was conducted using field emission scanning electron microscope (FESEM) Model Quanta FEG 450 with image analyser at various magnifications while the elemental compositions was obtained using Bruker elemental analyser.

RESULT AND DISCUSSION

1. XRD Analysis

The XRD pattern of as synthesized Ag NPs is shown in Fig.1

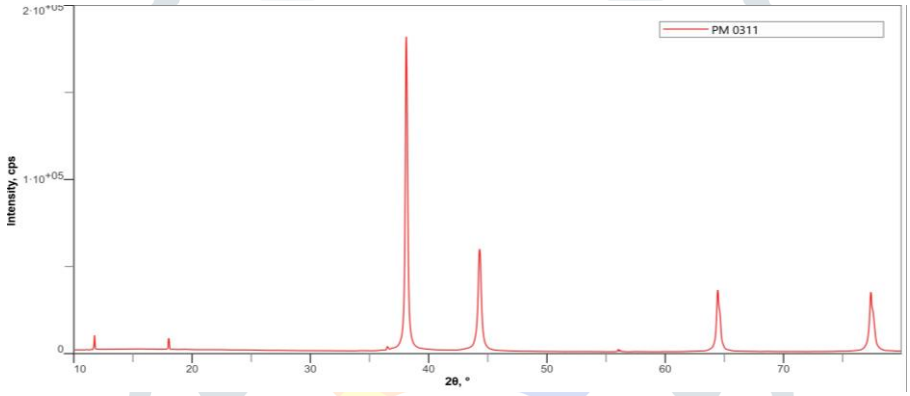

Fig. 1. XRD of as synthesized AgNPs.

The peak intensity is sharp, intense and narrow, confirming that AgNPs are with good crystallinity and fine grain size. These peaks are matched with the face centered cubic (fcc) structure of silver, (JCPDS data file No. o4-0783). Four peaks at 2θ values of 38.11, 44.31, 64.44, 77.38 degrees which corresponds to (111), (200), (220) and (311) planes of Silver. The detail XRD analysis of AgNPs is represented in Table 1.

Table 1: XRD analysis of AgNPs

(hkl)	2θ	θ	Cos θ	Sin θ	FWHM degree	β radian	D nm	d Å	a Å
111	38.11	19.055	0.9452	0.3265	0.2508	0.0044	**34.90**	2.3558	3.8396
200	44.31	22.155	0.9261	0.3771	0.3814	0.0067	23.42	2.0419	3.8388
220	64.44	32.220	0.8460	0.5332	0.3820	0.0067	25.60	1.4441	3.8396
311	77.38	38.690	0.7805	0.6251	0.2769	0.0048	38.27	1.2298	3.8390

The crystalline size, d-spacing values, and lattice constant all confirms the sample to be silver crystalline particles. The crystalline size (D) from the intense peak is **34.90 nm** while the mean crystalline size is 30.58 nm. using Debye-Scherrer formula [14,15] confirming the nanoparticle nature of the obtained sample by reduction.

2. UV-Vis spectroscopy

Silver nanoparticles appear grey in Color in aqueous medium as a result of surface Plasmon vibrations. The reduction of pure silver nanoparticles was confirmed by the UV-Vis spectra of the reaction medium. The UV-Vis spectrum of silver nanoparticles is shown in **Fig.2**.

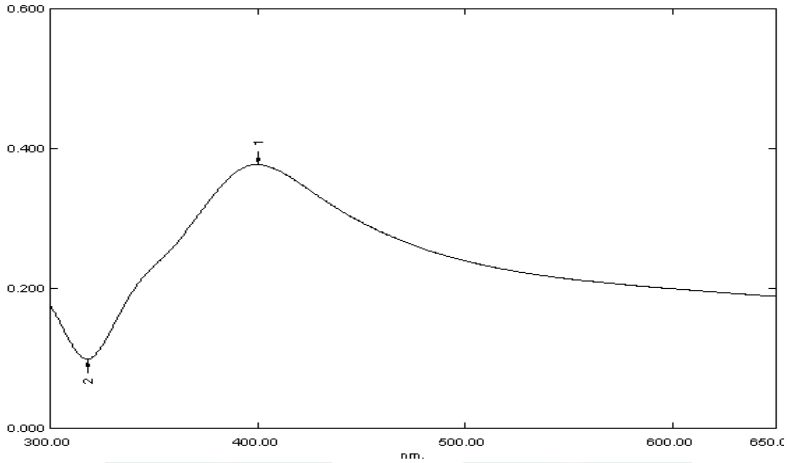

Fig.2. UV-Vis absorption spectrum of grey colloidal AgNPs.

The spectroscopic band of silver nanoparticles solution was found to be at 408 nm which confirms the synthesis of silver nanoparticles. This absorption strongly depends on the particle size and chemical nature.

3. FT-IR spectrum

The functional group present in the compounds can be determined using resultant spectra. A FT-IR study was carried out and the spectrum is shown in **Fig.3**.

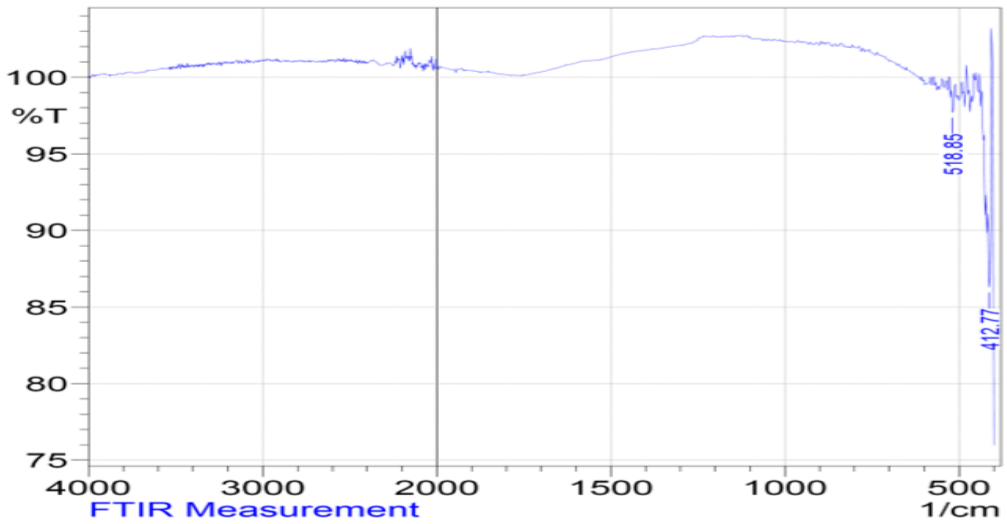

Fig.3. FT-IR of AgNPs.

FT-IR shows intense peaks at 400 to 600 cm $^{-1}$. The two obvious infrared bands are observed at 416 cm^{-1} and 512 cm^{-1} which confirms the presence of silver metal.

4. FESEM analysis

Shape and morphology of the synthesized nanoparticles were identified FESEM analysis. The nanoparticles were examined under various magnifications. FESEM images of synthesized AgNPs are shown in **Fig.4.** It shows relatively spherical and hexagonal shaped nanoparticles.

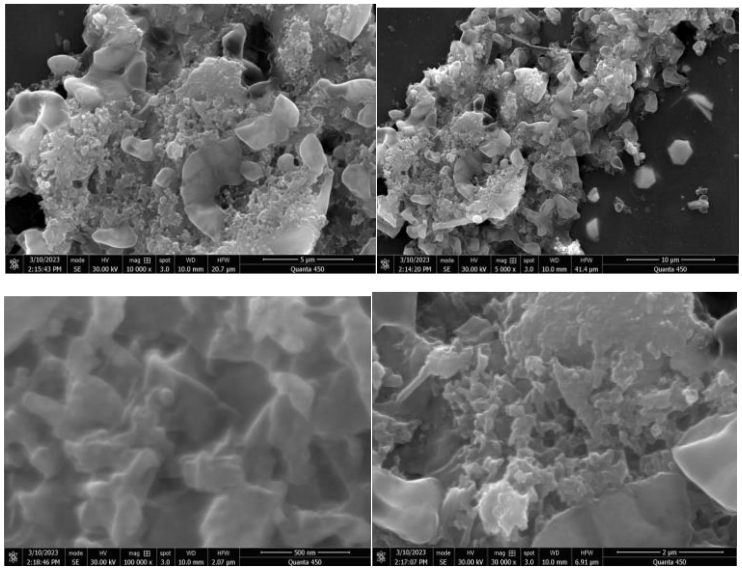

Fig.4. The FESEM images of synthesized AgNPs.

5. EDX analysis

The Energy Dispersive Spectroscopy (EDX) was used carry out the elemental analysis of silver nanoparticles. **Fig.5.** shows the EDX spectrum for elemental analysis of Silver Nanoparticles prepared by chemical method.

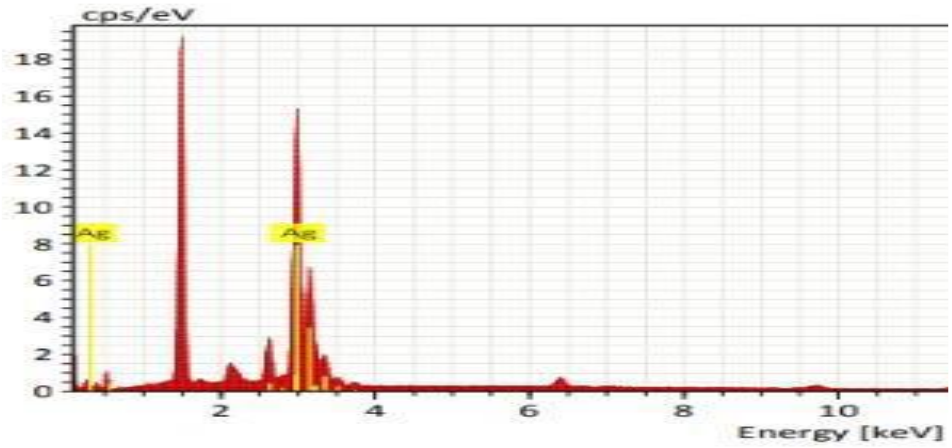

Fig. 5. EDX for elemental analysis of AgNPs.

In above EDX spectrum the vertical axis displays the number of X-ray counts while the horizontal axis displays energy in keV. Identification of the characteristic and distinct lines for the major emission energies of elemental Silver displayed and these correspond to peaks in spectrum.

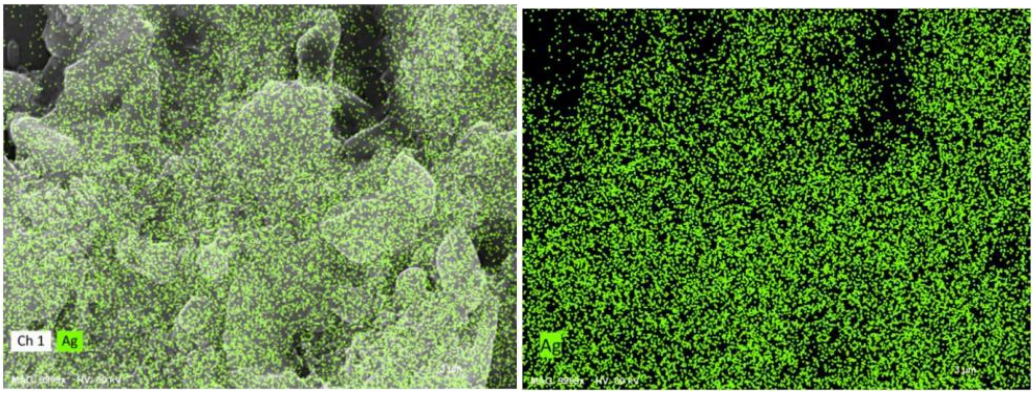

Fig. 5. EDX images for elemental analysis of AgNPs.

These observations give confidence that the silver metal has been correctly identified in as prepared AgNPs.

APPLICATIONS

1. Catalytic activity of as synthesized AgNPs in organic synthesis

A) Synthesis of diazobenzene through oxidative coupling of aniline:

Synthesis of diazobenzene was achieved by using aniline, KOH in DMSO in the presence of synthesized AgNPs. Due to higher activity, convenient synthesis and reactivity, very little quantity of AgNPs is required as model catalyst.

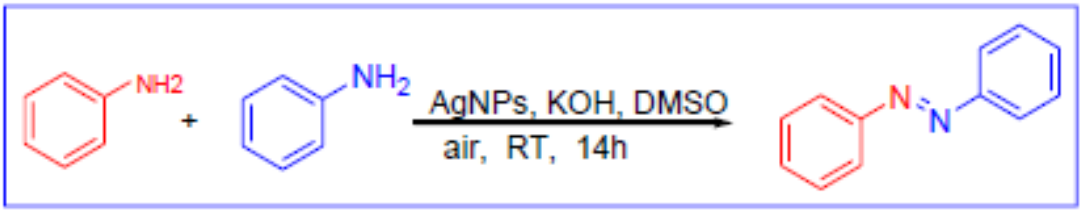

Fig. 6. Synthesis of diazobenzene by oxidative coupling of aniline with AgNPs.

Procedure for synthesis of Azobenzene:

In 10 ml RB flask, aniline (1 mmol), KOH (1 equiv.) and AgNPs (6 mmol) were added in 5-10 ml of DMSO and stirred at 60°C for 14 hours. The progress of reaction was monitored by TLC.

Mechanism: Silver nanoparticles were used for oxygen activation as shown in below:

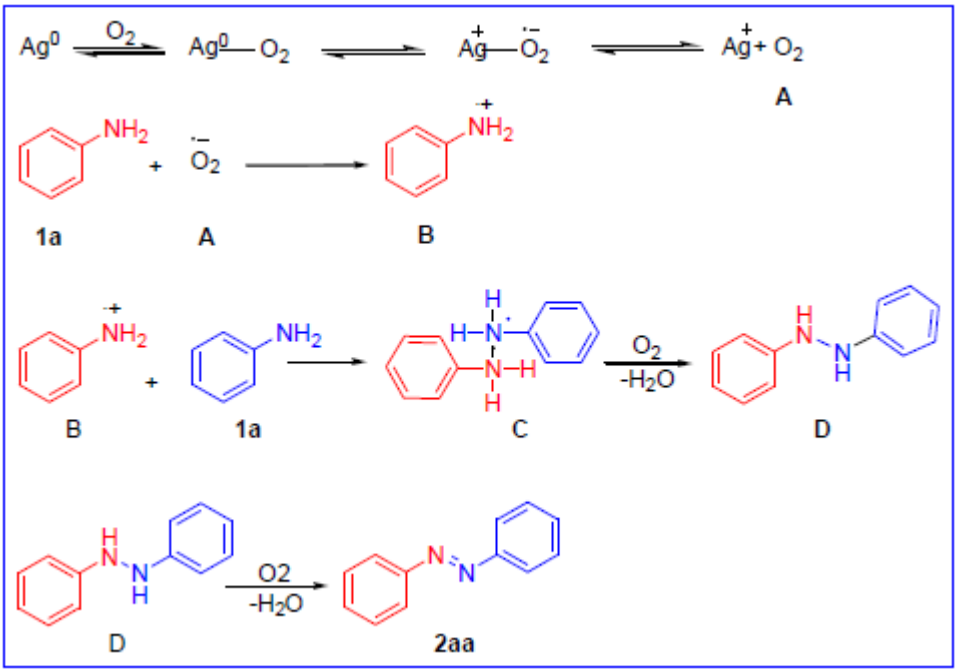

Fig. 6. Mechanism for synthesis of diazobenzene catalysed by AgNPs.

Characterization of Diazobenzene

The FTIR spectrum of as synthesized azobenzene is shown in Fig.7. A peak at 1496 cm^{-1} is results from the stretching of the N=N bond and it indicates formation of diazo compound. The absorption peak at 1683 cm^{-1} indicate that C=C stretching. The peak at 3338 cm^{-1} shows -CH bond stretching. The absorption peak at 1018 cm^{-}

[1] could be assigned for the presence of C-N stretching. The band at 1598 cm^{-1} shows the presence of aromatic ring.

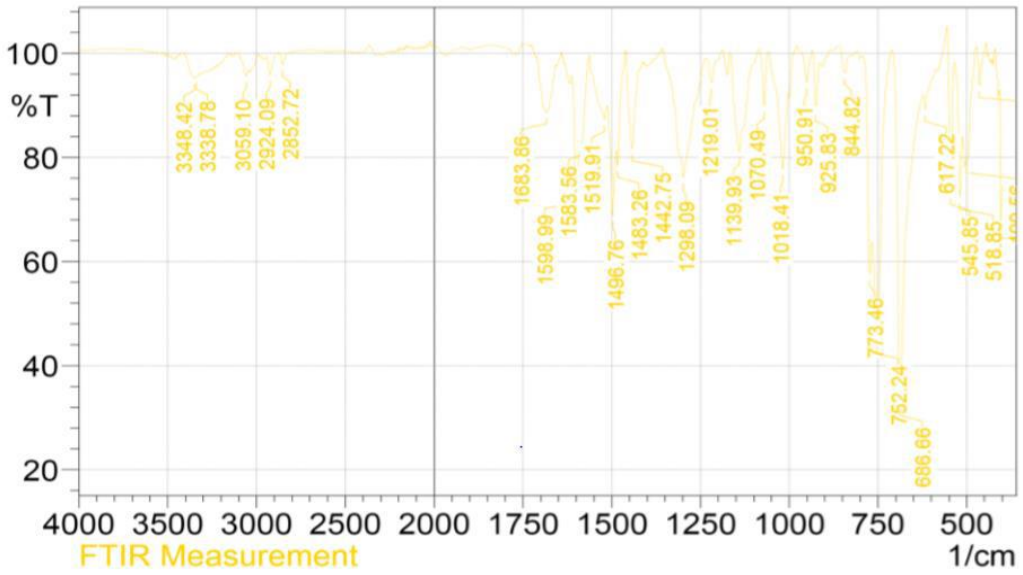

Fig.6. FT-IR of as synthesized Diazobenzene

B) Synthesis of β-Enamino Ester using AgNPs as a catalyst:

Procedure for synthesis of β-Enamino Ester:

In 10 ml RB flask, ethyl acetoacetate (1 mmol), aniline (1 mmol) and AgNPs (0.2 mmol) were added in 4-5 ml methanol and stirred at 60ºC for desired time. The progress of reaction was monitored by TLC. It confirms formation of β-Enamino Ester catalysed by AgNPs.

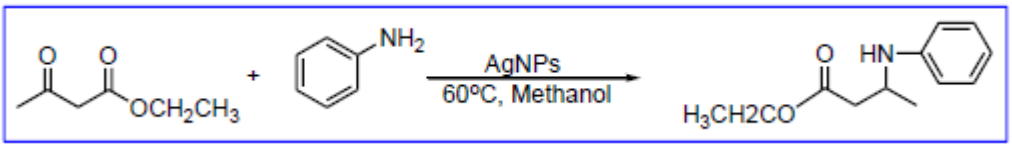

Fig. 7. Synthesis of β-Enamino Ester catalysed by AgNPs.

2. Metal sensing performance

The sensing performance of as synthesized AgNPs towards various heavy metals, like, Ni (II), Cu (II), Mg (II), Zn (II), was carried out by simple method. For this purpose, in 1 ml of metal ion solution (0.01 mg / ml), 1 ml of AgNPs colloidal solution was added. The distinct colour changes are observed due to addition of the AgNPs colloidal solution as shown in Fig. 8.

Fig.8 (a) Images of aqueous solution of different metals

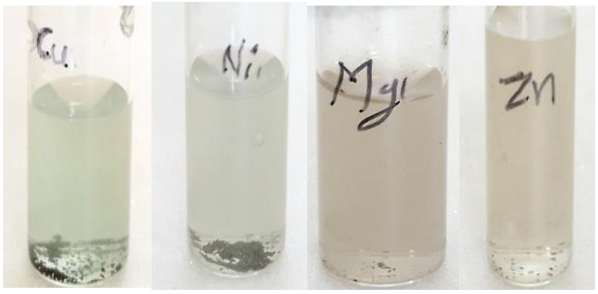

Fig.8 (b) Images of colour changes observed after addition AgNPs colloidal solution

The absorbance of each solution was measured against a blank solution in the range of 300-700 nm after being kept at room temperature for 10 min using UV-VIS spectrophotometer.

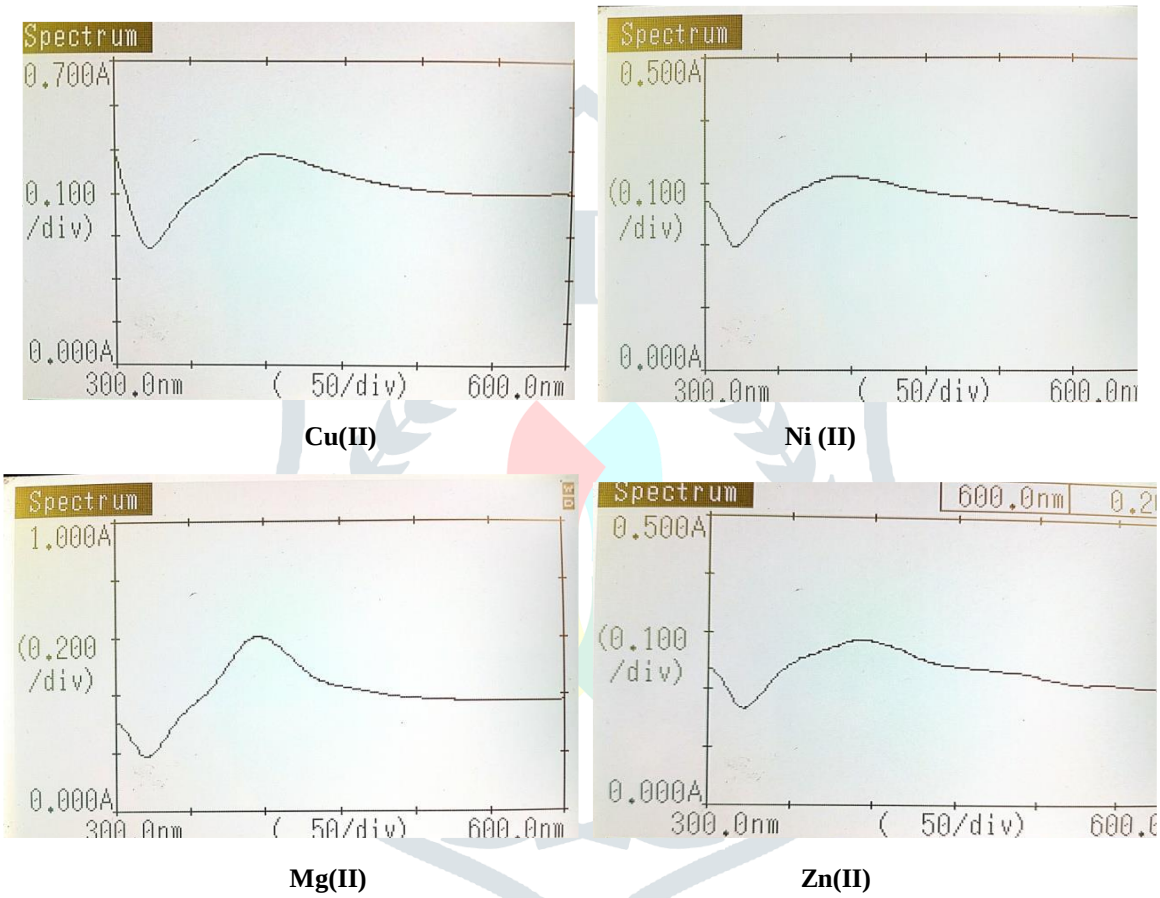

Fig.8. The UV-VIS spectra of metal ions after addition of AgNPs colloidal solution.

CONCLUSION

Chemical synthesis of AgNPs was successfully carried out by reduction of $AgNO_3$. It is safe, economical and simple approach which require less time. The presence of well dispersed crystalline, spherical AgNPs of size ~ 21 nm were confirmed by XRD, UV-VIS, FESEM, EDX and FTIR analysis. Thus synthesized AgNPs could provide an instant and safer catalytic activity for various routes in organic synthesis, which can complete in less time with appropriate yield. Also, as synthesized AgNPs are employed for heavy metal sensing purpose with a very simple, economical and fast naked-eye detection. This may be an alternative method for screening metal ions in water purification and pharmaceutical quality assurance.

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Conflicts of interest: The authors declare no conflict of interest.

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