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STRUCTURAL, OPTICAL PROPERTIES OF GREEN SYNTHESIZED SILVER NANOPARTICLES AND THEIR CATALYTIC ACTIVITY

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Abstract:

The rapid, extracellular formation of silver nanoparticles by green, low cost, energy conservative route using *Aspergillus flavus* at different pH values are reported in this article. The surface plasmon resonance of the silver nanoparticles synthesized at different pH values was studied visually and then by using UV-visible spectrophotometer. Silver nanoparticles prepared at pH value 9 were subjected further for XRD, SEM, TEM and photoluminescence characterization. X-ray diffraction pattern showed the peaks at 37.4^0, 44.5^0, 64.4^0, and78^0which are indexed to the (111), (200), (220) and (311) planes respectively indicating the crystalline nature of the nanoparticles with face centred cubic structure. A single peak in the UV-visible spectra specifies that the particles were spherical in shape which was also confirmed from SEM and TEM micrographs. Fluorescence emission maxima were recorded at 543 nm when excited at 420 nm. The synthesized silver nanoparticles revealed excellent catalytic activity in the reduction of Methylene blue by $NaBH_4$.

KeyWords: Silver Nanoparticles, SPR, UV-Visible Spectra, XRD, SEM, TEM, PL and Catalytic Activity

1. Introduction:

Nanoparticle is an assembly of atoms or molecules in the size range between 1 to 100 nm. For small particles, the electrical [1], thermal [2], optical [3, 4] properties can be tailored by changing the size and shape of the nanoparticles. The reactivity of the metal nanoparticles increases as the size of the particles decreases which happens due to increase in number of atoms at the surface of the particle. Due these unique and fascinating properties of the metal nanoparticles, their applications are continuously increasing in various fields like catalysis [5], electronics [6], optics [7], medicine [8] and food packing [9] etc. The optical properties of the metal nanoparticles depend on the surface plasmon resonance phenomenon which is the collective oscillation of free electrons of metal nanoparticles in resonance with the incident photons. The SPR absorption maxima and the bandwidths are sensitive to size, shape, nature and composition of the dispersion medium [10, 11, 12] and particle size distribution [13]. Organic dyes released from textile, plastic, medicine and various other industries are the main causes for waste water pollution. In such cases the conventional water treatment methods are not effective and hence the metallic nanocatalysts can be employed to remove these dyes from the water [14]. The use of silver for the treatment of burns and chronic wounds has been known for a long time. Now much attention of researchers is turned towards the study of silver nanoparticles because 1) they exhibit good antimicrobial activity against bacteria, fungi and viruses [15,16,17] , 2) the optical properties of the silver nanoparticles can be tailored by manipulating the size and shape of the nanoparticles, 3) they possess low toxicity to human cells [16] , high thermal stability [18] and low volatility 4) large scale production of silver nanoparticles is possible by green synthesis method[19] , 5) they exhibit excellent catalytic activity [20,21].

M. D. Balakumaran [22] synthesized silver nanoparticles using *Aspergillus Terrus*at different pH values and showed that the intensity of the brown color was increases with increase in pH value. Thus, the phenomenon of SPR is the function of the pH value of the reaction medium. The silver nanoparticles synthesized by using syzigiumcumini leaf extract [5] showed good catalytic activity for the reduction of para nitro phenol to para amino phenol.

In the present investigation we report the rapid, extracellular synthesis of silver nanoparticles under alkaline environment and synthesized silver nanoparticles which were found to be more stable. To the best of our knowledge there was no report in the literature for the *Aspergillus flavus* synthesized silver nanoparticles for their catalytic activity. Here we have reported the preparation of silver nanoparticles using *Aspergillus Flavus* and their catalytic performance for the reduction of methylene blue by $NaBH_4$.

2. Experimental Procedure:

2.1 Chemicals and Ingredients: Chemicals, silver nitrate and 1N Sodium hydroxide were of analytical grade. Potato dextrose broth was of HI Media. The fungus culture *Aspergillus flavus* was obtained from National Chemical Laboratory culture collection centre, Pune.

2.2 Synthesis of Silver Nanoparticles: The fungus *Aspergillus flavus* was grown in potato dextrose broth under static condition at 30± 2^0C for seven days. The biomass was then separated by filtration using Whatmann No.1 filter paper. The biomass was washed two or three times so that no trace of media component remains with it and then resuspended in 100ml deionized water and incubated at 110 rpm at 30 ± 2^0C for 96 hours. The cell filtrate then obtained was used for further reactions. Four flasks each containing equal amount of cell filtrate and 1mM $AgNO_3$ solution but having the pH value 6,7,8,9 respectively were kept in orbital shaker and incubated at 110rpm at temperature 30 ± 2^0C. The silver nanoparticles prepared at pH value 9 were further characterized for XRD, SEM, TEM, PL and their catalytic performance was evaluated.

2.3 Characterization of Silver Nanoparticles:

2.3.1 Effect of pH:

Visual Observation: Change in colour of different samples was visually observed at different time interval.

UV-Visible Spectroscopy Analysis: UV-visible spectroscopy is the technique used to determine optical properties of silver nanoparticles. The UV-visible spectra of the different samples were recorded using Shimadzu2450 spectrophotometer in the range 200 nm to 800nm.

2.3.2 X-Ray Diffraction Analysis: The colloidal solution of silver nanoparticles was obtained in powder form which then subjected to X- ray diffraction analysis.

2.3.3 Scanning Electron Microscopy: Thin films of the silver nanoparticles were obtained on glass slide from the colloidal solution of the prepared silver nanoparticles and these films were used for SEM characterization.

2.3.4 Transmission Electron Microscopy Analysis: TEM analysis was carried out using Philips CM 200 Transmission Electron Microscopy.For TEM measurement drop of aqueous solution of silver nanoparticles was placed on the carbon coated copper grid and dried by allowing water to evaporate at room temperature.

2.3.5Photoluminescence Spectra: Perkin Elmer LS 55 Spectro-fluorometer was used to record the photoluminescence spectra of the synthesized silver nanoparticles. Both the excitation and emission slit widths were kept at 5 nm. The entire scanning was done at 100 nm per minute.

3. Catalytic Activity:

The catalytic performance of the synthesized silver nanoparticles was observed visually and by using UV-visible spectrophotometer. For this purpose, two test tubes A and B were taken. Each tube contain mixture of 2ml methylene blue and 0.5 ml of $NaBH_4$ solution. In the tube B, 0.3 ml of silver nanocatalyst was added. The procedure was similar as described by Kaithavelikkath Francis Princy and et.al [21].

4. Result and Discussion:

4.1 Visual Observation: The change in colour from yellowish to brown indicates the probable formation of silver nanoparticles. The change in colour can be attributed to the surface plasmon resonance of formed silver nanoparticles [23].

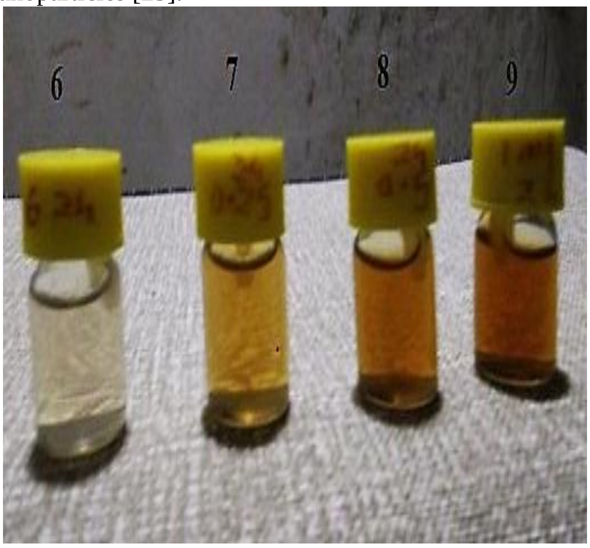

Figure 1 (a): Cell filtrate at different pH values after 6h

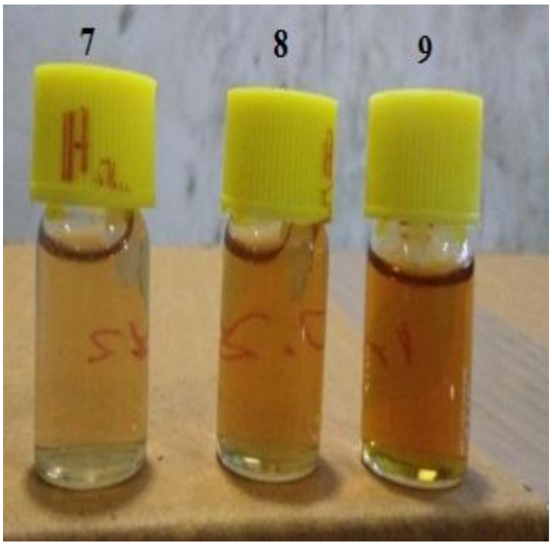

Figure 1 (b): Cell filtrate at different pH values after 12h

Figure 1a. depicts the cell filtrate treated with 1mM silver nitrate solution at pH values 6, 7,8,9 from left to right after 6 h and Figure 1b. Showed the results for the pH values 7, 8, 9 after 12h. It is observed that the intensity of the colour was increases with increase in time and the pH value. For the pH value 9 the brown colour attains the maximum intensity after 12 h indicating the complete formation of silver nanoparticles. For the pH value 6 the cell filtrate maintains the same colour evenafter 72h.

4.2 UV-Visible Spectroscopy:

Figure 2represents the UV-visible spectra of synthesized silver nanoparticles corresponding to pH values 7, 8, 9. The SPR bands appeared between 418 nm to 427 nm representing the characteristic signature of the silver nanoparticles. Rapid and optimum production was obtained at pH value 9 for which SPR absorption band is narrow and peak at maximum. The appearance of the single band indicates the formation of spherical particles. For pH value 7 and 8 the SPR absorption band shifts towards longer wavelength and broaden which may be due to aggregation of particles.

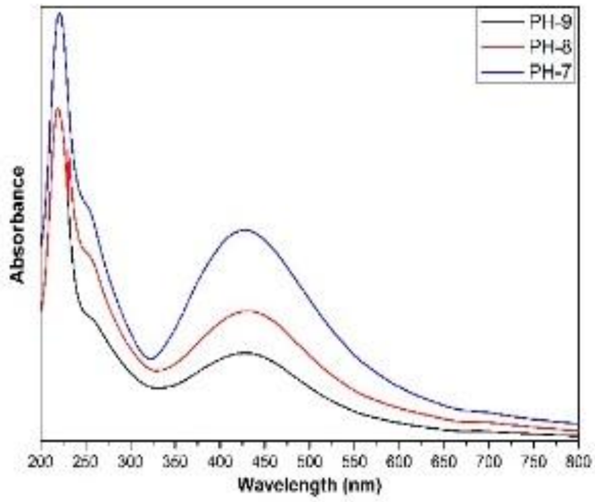

Figure 2: SPR peaks of Ag NPs after 12h

4.3 X-Ray Diffraction Analysis:

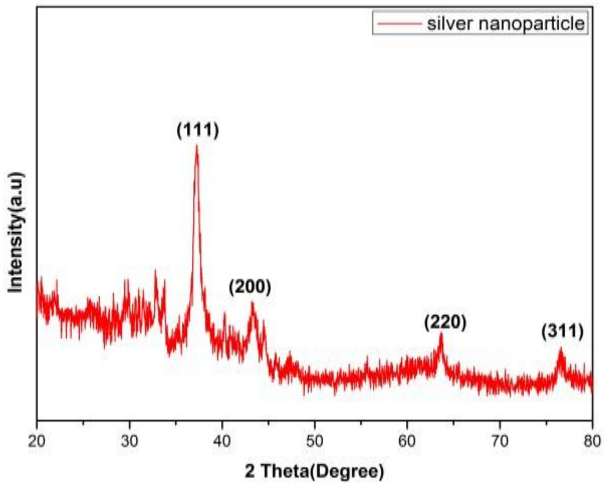

Figure 3: XRD pattern of Ag NPs

The XRD pattern of the prepared silver nanoparticles is depicted in the figure 3. The diffraction peaks observed at 37.4^0, 44.5^0,64.4^0, and 78^0corresponding to planes (111), (200), (220), and (311) respectively indicate the crystalline nature of silver nanoparticles with fcc geometry.

4.4 Scanning Electron Microscopy:

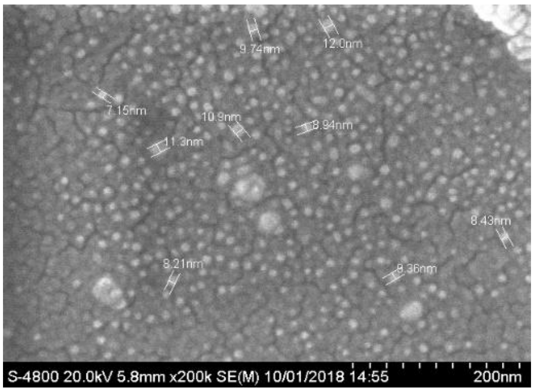

Figure 4: SEM images of Ag NPs

Figure 4 depicts the SEM micrograph of the silver nanoparticles which shows thatprepared particles were spherical and in the size range 5 nm to 12 nm.

4.5Transmission Electron Microscopy:

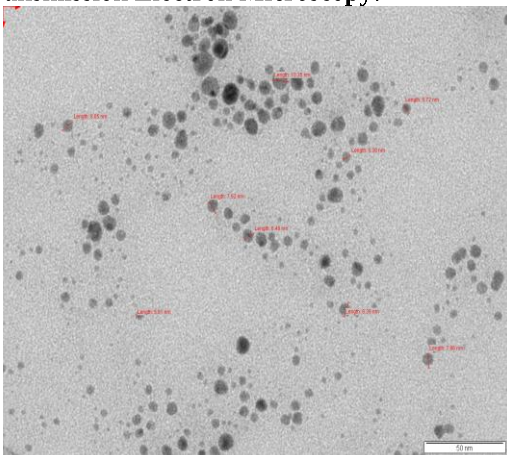

Figure 5(a): TEM images of Ag NPs

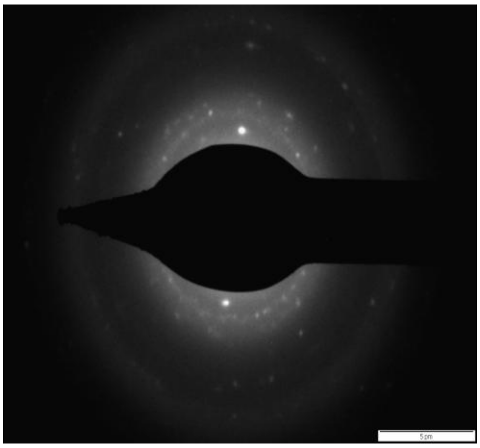

Figure 5(b): SAED pattern of Ag NPs

TEM micrographs shown in figure5 (a) revealed the morphology and size details of the synthesized silver nanoparticles. The particles were spherical in shape and in the size range between 5 nm to 11 nm. Surface area electron diffraction pattern shown in figure 5(b) signifies the face centred cubic geometry of the synthesized silver nanoparticles.

4.6Photoluminescence Spectroscopy: Photoluminescence spectra of the prepared silver nanoparticles are shown in the fig.6. It showed the emission peak at 543 nm when excited at 420 nm.

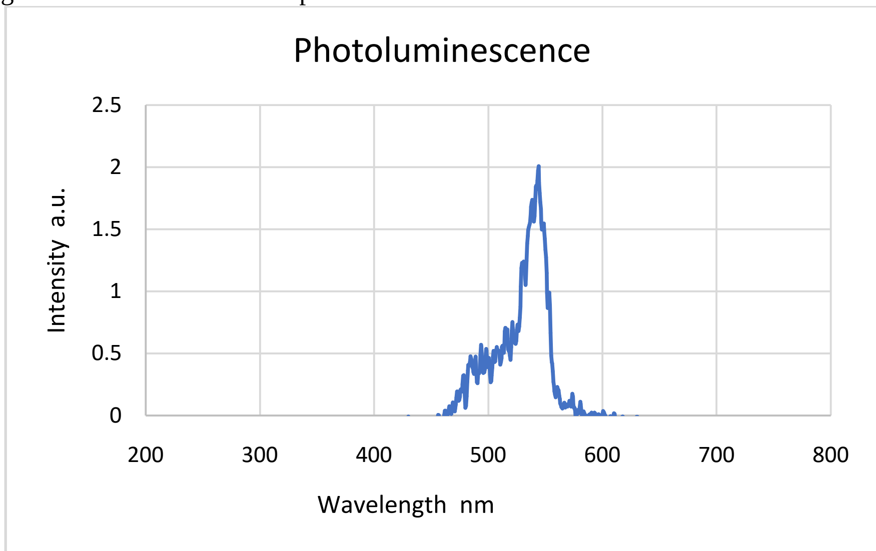

Figure 2: PL spectra of Ag NPs

5.0 Catalytic Activity:

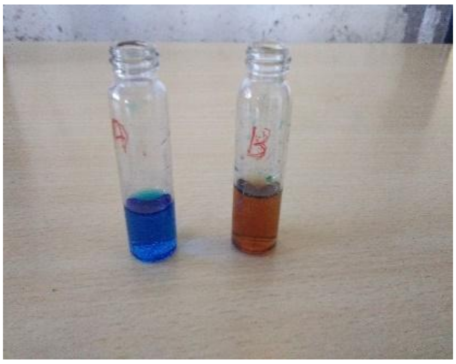

Figure 7: (A) M.B and (B) after reduction it by $NaBH_4$ in presence of Ag NPs

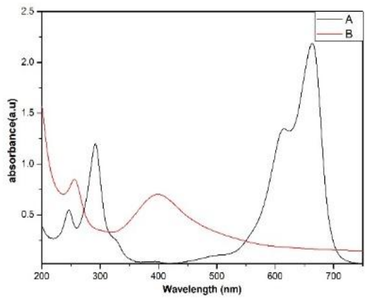

Figure 8: UV-visible spectra of reduction reaction

Methylene blue was deep blue in colour (Fig.7 A) and its absorption peak was appeared at 664 nm as exposed in figure 8 (A). When the silver nanocatalyst of 0.3ml was poured in tube B, the reduction starts immediately and the mixture becomes colourless in 90 seconds while the solution mixture in A remains blue in colour even kept for several hours. Thus, visually also we detect the reduction of MB. The peak obtained at 664 nm was immediately falls and new peak was obtained at 420 nm figure 8(B) which may be due to silver nanoparticles.

6. Conclusion:

Alkaline pH of the cell filtrate is favourable for the rapid extracellular synthesis of silver nanoparticles. Optical properties such as SPR of the silver nanoparticles are size dependent.The SPR bandwidth is decreases with decrease in the particle size. XRD and SAED pattern showed that the silver nanoparticles are crystalline in nature with fcc structure. SEM and TEM images revealed that the particles were spherical and in the size range 5 nm to 12 nm. The *Aspergillus* synthesized silver nanoparticle showed excellent catalytic activity. PL spectra proves the photonic property of the silver nanoparticles. The silver nanoparticles can be used for catalytic activities.

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