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Light Induced Green Synthesis of Silver Nanoparticles Using Aqueous Extract of *Prunus amygdalus*

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Abstract

Light driven, photon mediated green synthesis of silver nano-particles (AgNPs) was carried out using aqueous silver nitrate solution (1 mM) and aqueous extract of almond (*Prunus amugdalus*). Experiments were carried out in dark, diffused sunlight and direct sunlight to study the influence of light intensity as well as by wrapping the reaction tubes with colored cellophane filters (violet, green, yellow and red) to investigate the effect of light color on AgNP synthesis. It was observed that the violet filter enhanced the AgNPs synthesis appreciably. The FTIR spectroscopic analysis confirmed participation of bio-molecules with hydroxyl and amide groups present in the almond extract as reducing and capping or stabilizing agents, respectively. Dynamic light scattering (DLS) studies revealed the particle size distribution of nano-particles as 2 – 400 nm, and scanning electron microscopy (SEM) confirmed their spherical shape with an average size of about 20 nm. Growth analysis of AgNPs revealed an increase in number of nano-particles with time, whereas their rate of growth decreased gradually. The AgNP suspension was stable even beyond 3 weeks.

Keywords

AgNPs, Nano-Particles, Green Synthesis, *Prunus amulgdalus*

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1. Introduction

The most commonly used methods for nano-particle synthesis such as chemical reduction [1], gamma-ray irradiation [2], micro-emulsion [3], laser ablation [4], electrochemical reduction [5], autoclaving [6], microwave irradiation [7] and photochemical reduction [8] are associated with one or the other disadvantages like toxicity, high operation cost and energy inefficiency, and thus raising many environmental concerns. The quest for environmental friendly and sustainable methods to synthesize AgNPs has gained momentum during the past decade and shifted the interest of the researchers towards the bio-reduction potential of microorganisms [9]-[12], and plant extracts [13]-[20]. Natural polymers have also been used as reducing and capping agents in the synthesis of nano-particles [21]-[24]. The eco-friendly green synthesis methods suffer from the drawback of longer synthesis period for generation of AgNPs [25]. The vital need for efficient and cost effective supplementary methods to reduce the reaction time lag has attracted the interest of the researchers on light driven plasmon mediated reactions [26]. The photon induced methods are gaining increasing interest due to their advantages like controlled reducing action and generation of uniform AgNPs, capability to get absorbed by molecules without any additional absorption promoters and their low cost [27].

In the present work, aqueous extract of *Prunus amygdalus* was used to produce AgNPs, whose synthesis is mediated by the photons present in the sunlight. To the best of our knowledge, this is the first report regarding synthesis of AgNPs using aqueous almond extract.

2. Materials and Methods

2.1. Materials

Silver nitrate of 99.8% purity (Ranbaxy Industries Limited, India), fresh almonds (obtained from the local market of Varanasi, U.P) and distilled water was used in the experiments. Colored cellophane papers were purchased from the stationery market and all glass wares used in the experiments were purchased from Borosil (ISO 9001) Company, India.

2.2. Preparation of AgNPs

Almond extract was prepared by soaking 20 g of washed almonds in 100 ml distilled water for a period of 24 hr at 20˚C followed by filtration using a Whatman's filter paper. This filtered aqueous extract (30 ml) was added to 30 ml aqueous $AgNO_3$ solution (2 mM) in a volumetric flask (250 ml) for a final concentration of 1mM ($AgNO_3$). The above experiment was carried out in triplicate and the reaction mixtures were kept under dark (no light), dispersed sunlight and direct sunlight conditions. The above samples were stored and subjected to optical characterization studies.

In another set of experiments, AgNPs using similar reaction mixtures were synthesized in test tubes wrapped with violet, green, yellow and red colored cellophane papers, with 3 min exposure to direct sunlight. These samples were subjected to optical characterization study and results were recorded.

A typical sample of AgNPs of similar proportion was also synthesized with 3 min exposure to sunlight and was stored for optical, functional and morphological analyses. In order to carry out SEM analysis, the sample was centrifuged at 10,000 rpm for 10 min and the particles settled at the bottom of the tube were collected.

2.3. Characterizations

Synthesized AgNPs were subjected to optical analysis using PC based double beam UV-Visible spectrophotometer (Model-2202, Systronics) operated at a bandwidth of 2 nm in the wavelength range of 200 - 800 nm. Functional group analysis was carried out with a FTIR spectrophotometer (NICOLET-5700-Thermo Electron Corporation, USA) and morphological analysis was done using DLS (Delsa Nano C-Beckmann Coulter Company, Germany) instrument and SEM analysis performed using Supra-40, Carl Zeiss Oxford Instruments, Germany.

3. Results and Discussion

3.1. Effect of Light

UV-Vis spectral analysis of the samples grown under dark (no light) dispersed light and direct sunlight conditions

were carried out. Results (**Figure 1**) depict a remarkable difference in the absorbance patterns of the three cases, which reveals that no formation of AgNPs takes place under completely dark (no light) condition and the rate of formation of AgNPs gets accelerated by around 60 times in presence of direct sunlight compared to synthesis in dispersed light. The possible reason behind this behavior might the presence of greater number of photons of certain wavelength in direct sunlight which catalyzed the reducing action, thus promoting the formation of AgNPs.

UV-Vis spectral analysis of AgNPs synthesized in color wrapped reaction tubes (**Figure 2(a)**), to predict the effect of the wavelength of light promoting the AgNPs synthesis, revealed the highest absorbance for violet color (380 - 450 nm) wrapped tube (**Figure 2(b)**), proving that this portion of the visible spectrum promotes the AgNPs synthesis.

3.2. Surface Plasmon Resonance

The AgNps formation was accompanied by the appearance of yellowish-brown color from colorless sample (**Figure 3(a)**). Optical analysis of the sample revealed a Surface Plasmon Resonance (SPR) peak at ~420 nm (**Figure 3(b)**) due to the interaction of the electromagnetic radiation with the conduction band electrons around the nano-particles [28]. Sastry and coworkers also reported most of the SPR peaks of the AgNPs in the range of 400 - 450 nm [29].

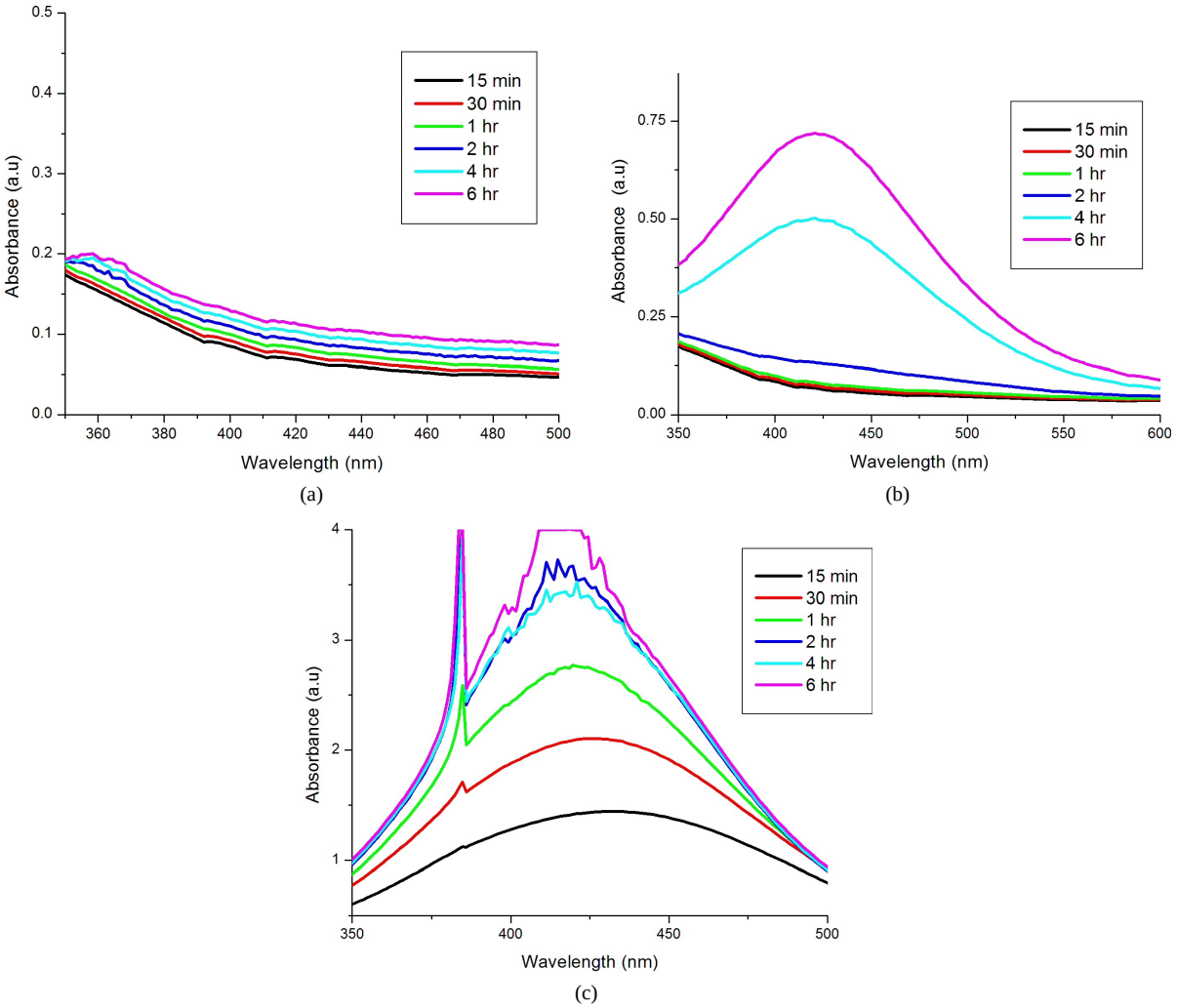
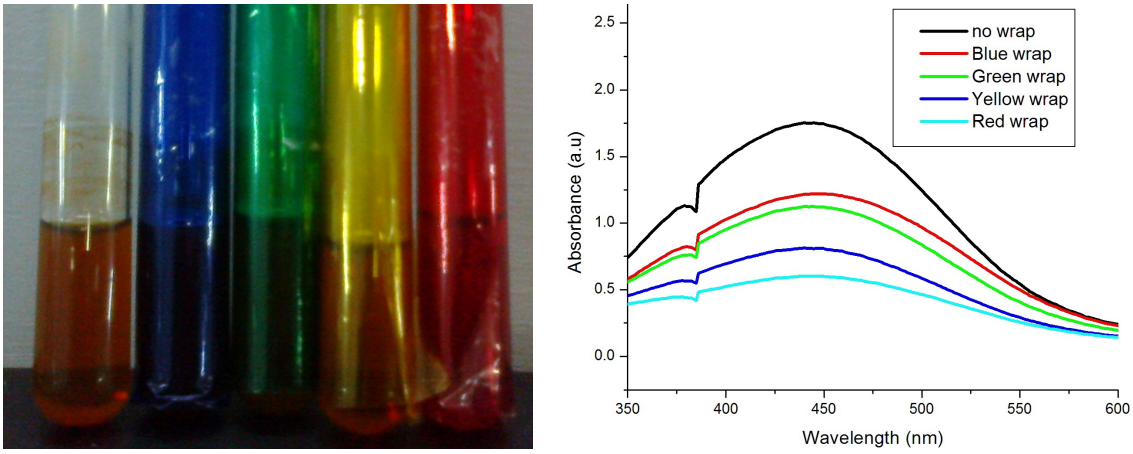
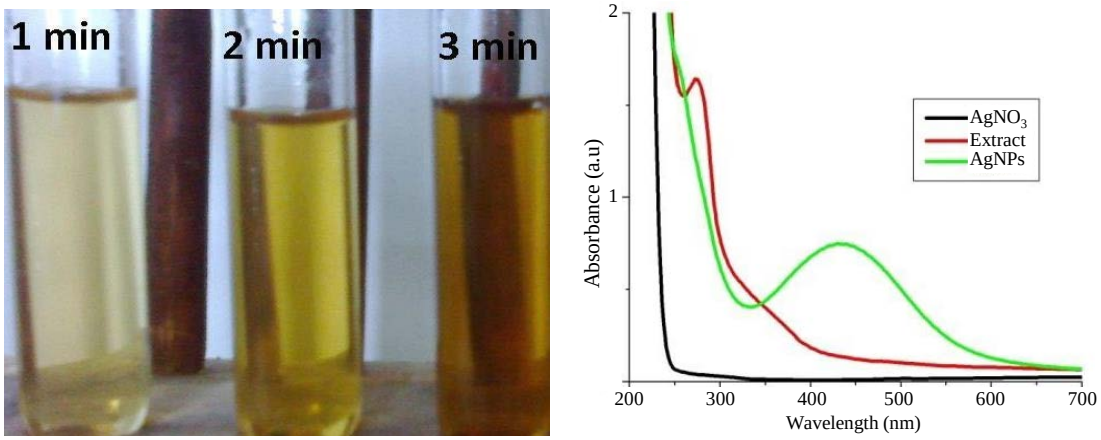


Figure 1. UV-Vis spectral analysis of AgNPs suspension samples (a) No light, (b) Exposed to dispersed sunlight (normal room light), (c) Exposed to direct sunlight.



(a) (b)

Figure 2. Effect of light wavelength on AgNPs synthesis: a) Reaction tubes wrapped with colored cellophane papers, b) UV-Vis spectra of AgNPs suspensions at different wavelengths.



(a) (b)

Figure 3. (a) Visible color change of the aqueous extract due to AgNP formation after exposure to the sun light for various durations due to AgNPs formation and (b) change in their SPR Peak.

3.3. Functional and Morphological Analysis

The FTIR spectral results (**Figure 4**) revealed significant peaks for almond extract at 1636.4 cm^{-1} (amide-I and C = O), 3301.7 cm^{-1} (OH-stretch) and for AgNPs at 1636.3 cm^{-1} (amide-I and C = O), 3286.8 cm^{-1} (OH-stretch). Decrease in the wave number from 3301.7 to 3286.8 cm^{-1} after formation of AgNPs proved the consumption of OH groups for the synthesis, whereas no change in the wave number of amide group confirms their role in the stabilization of AgNP's. No significant change in the transmittance might be due to very low change in the concentration of active ingredient which is involved in changing Ag^{+} ions to AgNP and might also imply the presence of numerous number of reducing groups available in the biological extract (1636.4 cm^{-1}). The results are in agreement with observations made by other researchers [30]-[32].

The SEM and DLS analyses revealed that the AgNp's are ~20 nm spheres and the particle size varied in between 5 - 400 nm, with an average diameter of ~100 nm (**Figure 5**). Variation in the size estimate between the above two methods is due to the fact that the later method also measures the layer of water molecules associated with the AgNPs [33].

3.4. Growth Analysis

Change in absorbance of synthesized AgNPs suspension was analyzed for a period of 20 days. An increase in

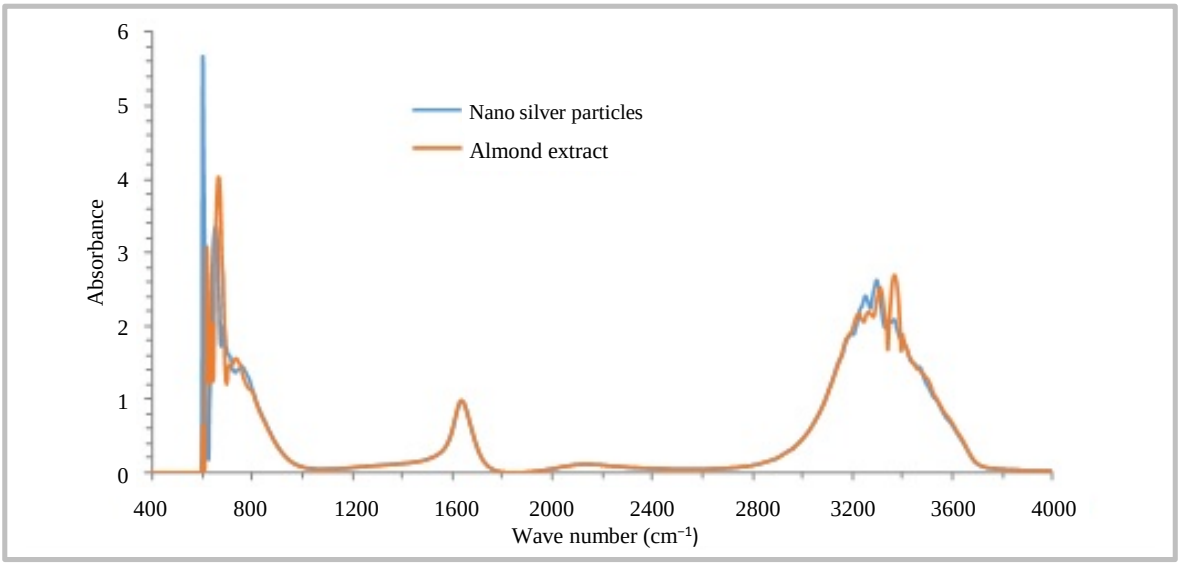
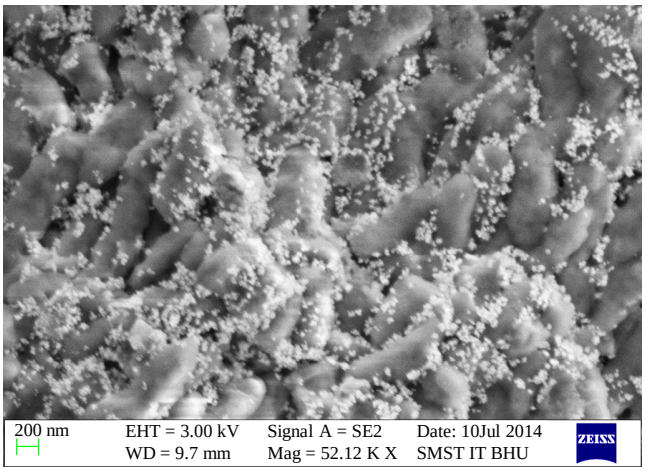


Figure 4. FTIR spectra of almond extract and AgNPs suspension.



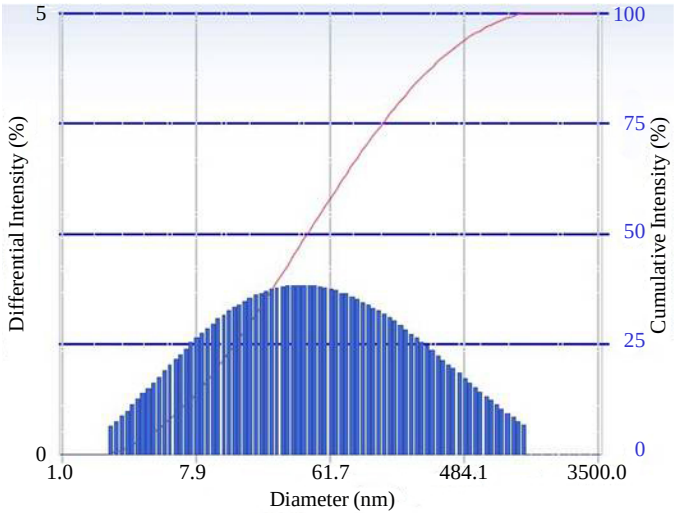


Figure 5. DLS spectra and SEM photomicrograph of AgNPs particles.

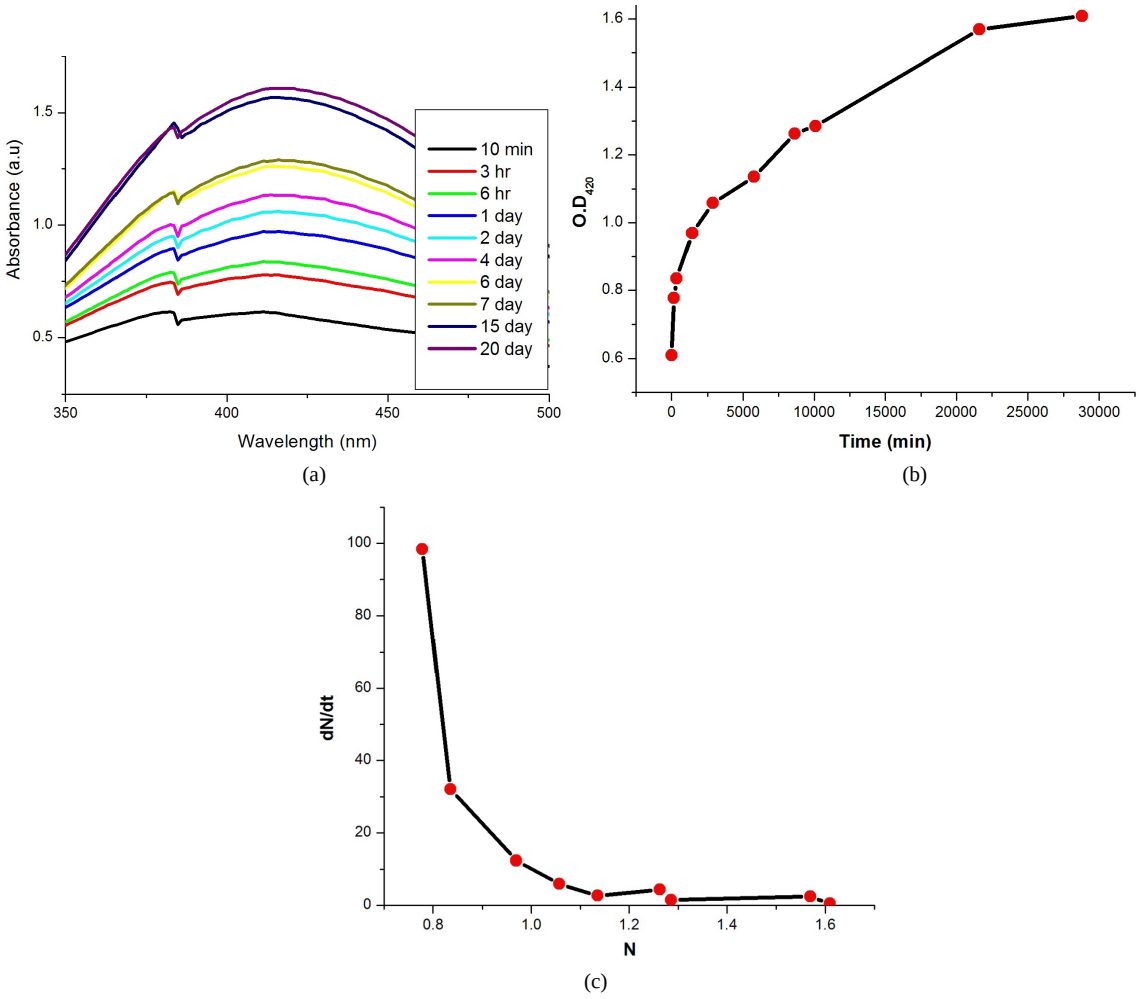


Figure 6. Growth Analysis for a period of 20 days, a) UV-Vis spectral analysis, b) Growth in number of AgNPs, c) Rate of formation of AgNPs.

absorbance (O. D_{420}) with increase in time period signifies the growth in the number of AgNPs (N). It is also observed that the rate at which the number of AgNPs being synthesized (dN/dt) was high during the initial days and a gradual decrease in this rate was observed leading to a constant rate or no new growth zone after 18 days (**Figure 6**).This behavior might be due to the limited availability of extract molecules for the reduction of silver ions or due to the limited availability of Ag^+ ions for the extract molecules.

Aging of nano-particles causes a red shift in the wavelength of SPR peak thereby proving their instability [34]. The synthesized AgNPs reported no wavelength shift in the SPR peak for a period of 20 days, proving their stability.

4. Conclusion

Aqueous extract of *Prunus amygdalus* is an effective biological agent for synthesizing stable (20 days) and spherical AgNPs (~20 nm). Alcoholic groups presented in the extract promote the AgNPs synthesis and amide groups promote the stabilizing action. Violet portion of visible light supports the synthesis of AgNPs. Sunlight, photo catalyzed the reducing action of biological agent and accelerated the synthesis rate by about 60 times. Growth analysis of AgNPs revealed that the rate of formation of nano-particles decreases gradually with time.

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