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Green synthesis of silver nanoparticles using soymida febrifuga: optimization, characterization and for dye degradation in photocatalytic activity via green way

Varsha. S. Nandeshwar[1,a], Surekha. A. Kalkar[1,b], Pratibha. S. Agrawal[2,c]

[1a]Reseach scholar, Department of Botany, Institute of Science, RTMNU, Nagpur (M.H) 440008, India.

[1a] Professor, Department of Botany, Institute of Science, RTMNU, Nagpur (M.H) 440008, India.

[2c] Professor, Department of Applied Chemistry, LIT, RTMNU, Nagpur (M.H.) 440033, India.

Email - [1]varshanandeshwar26@gmail.com

Abstract: *Traditional synthetic techniques for silver nanoparticles synthesis involve toxic chemicals that are harmful to humans as well as the environment. The green chemistry method for nanoparticle synthesis is rapid, eco-friendly, and less toxic as compared to the traditional methods. In the present research, we synthesized silver nanoparticles employing a green chemistry approach from Soymida febrifuga bark extract. The optimized Soymida febrifuga silver nanoparticles (SFAgNPs) had a mean particle size of 187.87 ± 4.89 nm with a narrow size distribution of 0.226 ± 0.009 and surface charge −34 ± 3.12 mV, respectively. The physicochemical characterization of optimized SFAgNPs was done by Fourier transform infrared spectroscopy (FTIR). These SFAgNPs were employed for the treatment of wastewater and dye degradation and so on.*

Key Words: *silver nanoparticles; soymida febrifuga; green chemistry; dye degradation*

1. INTRODUCTION:

Reported by S.S. Patil (2016) in their book "In the last few decades, anthropogenic activities and rapid industrialization have resulted into severe water pollution and thereby posing a serious threat towards human and ecological environment. In particular, organic and inorganic dyes with more than 7×10^5 tons annuals productions are the major toxic water pollutants. A large portion of it means more than 15% toxic and carsinogenic dyes is being discharged into water annually. However, only 47% of the synthetic dyes are biodegradable and generally require a significant attention due to their recalcitrance and hazardous characteristics. Even at low concentration, occurrence of dye affects the aquatic photosynthetic ecosystem and can be detrimental for aquatic lives as their growth can be inhibited by interfered sunlight in water bodies by organic dye molecules". Therefore green chemistry is the utilization of chemistry principles to minimize the usage of poisonous chemicals, minimal unwanted residues, which might be injurious to human health as well as to the atmosphere(1,2). A combination of green chemistry and nanotechnology is a versatile approach and has extended its consideration in the last few years (3,4). The green synthesis of nanoparticle (NPs), which is ecological and cost-effective and employs stabilizing agents attained from plant extracts and other natural resources for the fabrication of NPs without the usage of harmful compounds, also promotes the sustainable use of NPs (5,6). In the recent era, metallic NPs have been extensively used for various biomedical applications such as diagnosis, drug-delivery systems (DDs), and tissue engineering because of their exceptional physicochemical properties……(7,8). Among numerous metallic NPs, silver nanoparticles (AgNPs) have gained much attention for various applications, including imaging contrast agents, sensors, and antimicrobial agents owing to their better stability, electrical conductivity, and antimicrobial activity (9,10).

Also, AgNPs have shown their potential for the management of cancer. Many in vitro studies using AgNPs have proved their action as active anticancer agents against various cancer cells, including lung carcinoma, breast cancer, and human cervical cancer cells….. (11,12). Generally, AgNPs are synthesized via several chemical and physical approaches. The physical methods consist of ball milling, flame sonication, radiation, electric arc discharge, pyrolysis, etc.…….(13,14). These physical methods often require expensive instruments, higher pressure, and more energy consumption (9,11,15). Though, the chemical approaches frequently need expensive metal salts and harmful solvents. Moreover, different stabilizers are also essential to avoid the aggregation of NPs to make them physiologically compatible (16,17). In this context, green synthesis of AgNPs by plant extracts as a substitute method for the traditional physical and chemical NPs preparation methods…..(18,19).

Soymida febrifuga / Swietenia febrifuga (Roxb.) A. Juss. (Family-Meliaceae), generally bark used in the treatment of diarrhea, dysentery and fever and also as a general tonic, decoction used in gargles, vaginal infections, rheumatism swellings and as enemata. The deep red bark is very astringent and bitter. It is used in the treatment of diarrhea and dysentery, and is also often used as a febrifuge instead of quinine (Cinchona spp.) by local people. It is said to be an efficient remedy for the dangerous jungle fever of India when quinine produces no effect. It has also been employed successfully against typhus fever and has proven to be effective in treating bad cases of gangrene. But this Soymida plant not used for water treatment and dye degradation till now (20,21). Although conventional weed control methods are frequently used to manage this problematic plant, exploring its utility potential as an innovative management strategy is gaining attention nowadays (22,23). The plant is well-known for its primary and secondary metabolites, such as proteins, carbohydrates, tannins, volatile oils; especially lupeol, sitosterol, methyl angolensate, deoxyandirobin and 2 tetranortriterpenoids with a modified furan ring from the bark that contribute towards its allelopathic capacity, cytotoxic activity, and allergenic reactions (24,25). However, studies have reported that biochemical from Parthenium hysterophorus also have medicinal values such as antioxidant, anti-inflammatory, antibacterial, antifungal, and anticancer activities (26,27). There have been efforts in preparing NPs from the bark extracts of Soymida febrifuga, and further work was suggested to develop the value-added products of biomedical significance (28,29). But no study is performed yet for the optimized synthesis of AgNPs from this plant and also detailed therapeutic investigation of the so-formulated NPs has been investigated. The main objective of this study was the synthesis, optimization, and characterization of SFAgNPs from Soymida febrifuga, as well as the detailed study of their therapeutic activity, which to our best knowledge has not been done so far. For attaining this purpose in this study, we fabricated silver NPs using bark of Soymida febrifuga extract using a green chemistry approach. Synthesized SFAgNPs were characterized by UV. Vis spectroscopy, and the surface morphology of developed NPs was characterized by scanning electron microscopy (SEM) respectively. Moreover, the solid-state characterization had done by Fourier transform infrared spectroscopy (FTIR).

2. MATERIALS AND METHODS:

Preparation of Bark Extract

Fresh bark of Soymida febrifuga were collected from our campus Institute of Science, Nagpur (M.H.). Bark were thoroughly rinsed with tap water and then with double-distilled water. The bark were shade dried for 2-3 weeks. Uniform powder was made by passing the dry bark through a 50 mm sieve. To prepare bark extract, 10 g of bark powder was mixed with 100 mL distilled water followed by boiling at 80 ◦C for 30 min. Then, the extract was filtered by Whatman filter paper (No.1) and stored at 4 ◦C before being used to biosynthesize silver nanoparticles.

Figure 1. Bark of Soymida febrifuga plant.

Phytoreduction of Soymida febrifuga Silver Nanoparticles (SFAgNPs)

For silver nanoparticles synthesis, 1 mL of the Soymida febrifuga bark extract was added dropwise into 9 mL of freshly prepared 1 mM $AgNO_3$ solution with continuous stirring at room temperature for 30 min. The synthesis of nanoparticles was confirmed by reddish-brown color. After that solution was kept in the dark for a further 24 h allowing the complete reduction of the silver nitrate solution. UV-Vis spectrophotometry also confirmed the synthesis of silver nanoparticles. Lastly, SFAgNPs were collected by centrifugation at 10,000 × g rpm for 15 min by using optimized conditions (30,31). Different concentrations of $AgNO_3$ i.e., 0.5 mM, 1 mM, 2 mM, 3 mM, and 4 mM and bark extract i.e., 1 mL, 2 mL, 3 mL, and 4 mL and different reaction time i.e., 30 min, 1 h, 4 h, 6 h, 12 h, and 24 h were employed to standardize the optimum conditions.

Visual Inspection:

The color change after mixing silver nitrate with the plant extract in a suitable ratio is the first indicator of the formation of silver nanoparticles (32,33). The color change was monitored at various time intervals after reducing silver nitrate with Soymida febrifuga bark extract for checking the synthesis of SFAgNPs.

UV-Visible Spectroscopy:

The synthesis of silver nanoparticles was investigated by checking the absorbance of the diluted solution of silver nanoparticles suspension at a wavelength of 300–800 nm by a UV-Vis spectrophotometer. Silver nanoparticles exhibit strong electromagnetic wave absorption in the visible range owing to the surface plasmon resonance (SPR).

Scanning Electron Microscopy (SEM):

Morphology of the synthesized SFAgNPs was investigated by scanning electron microscope. For analysis, SFAgNPs were placed on glass slide following coating them with a thin layer of gold-palladium blend once mounted them on a carbon grid.

Fourier Transform Infrared Spectroscopy (FTIR):

FTIR analysis was used to scan the synthesized silver nanoparticles to obtain the capped functional groups on the nanoparticles. FTIR analysis of the Soymida febrifuga bark extract and synthesized nanoparticles was carried out using the KBr pellet method by the FTIR apparatus in transmittance mode from 400–4000 cm^{-1} at 4 cm^{-1}.

Treatment of Dye Degradation with under the photo catalytic activity Different dyes by SFAgNPs:

Synthetic dyes are extensively used in textile dyeing, paper printing, color imaging, pharmacy, food, cosmetics, leather industries and laboratory and so on. These dyes are poisonous and recalcitrant in nature due to their complex chemical structures. For better elimination of dye wastewater, efficient photocatalysts should be synthesized. Degradation of Acid orange 7 (AO7), often known as Orange II, Azo black (Chlorazole Black), Indigocarmine, Tartrazine, and Alizarine Red (10Tml/L) under UV light and visible irradiation by SFAgNPs. Dye degradation by catalysis becoming a key agent in self-care products, i.e., disinfectant or bleaching agents and broadly supplied in water or wastewaters.

3. **Results and Discussion :**

Visual Inspection

The change of color from dark brown to dark greenish in color, thereby visually confirmed the production of silver nanoparticles. Color change was observed within a half-hour of exposure (Figure 2). The change in solution color is due to the surface plasmon resonance (SPR) displayed by the bioreduced AgNPs (34,35). These results are in accordance with previously reported work (36,37)

Figure 2. Formation of Silver NPs from Soymida febrifuga

UV-Visible Spectroscopy

The ultraviolet-visible absorption spectrum of the synthesized SFAgNPs dispersion was examined between 300–800 nm through a UV-visible spectrophotometer. The spectrum of the SFAgNPs dispersion showed a single surface plasmon resonance absorption b and with a maximum of approximately 432 nm (Figure 3). As the symmetry of NPs increased, the number of SPR peaks decreased, and spherical SFAgNPs exhibited only one peak, while triangular and disc shape NPs showed two or more peaks. As the particle size increases, the SPR of the absorption spectrum of metal nanoparticles typically shifts to longer wavelengths (38,39). The effect of varying concentrations of silver nitrate and leaf extract and reaction time on the formation of SFAgNPs was also studied by periodically checking the absorbance of the reaction mixture through UV-Vis spectroscopy at 300–800 nm.

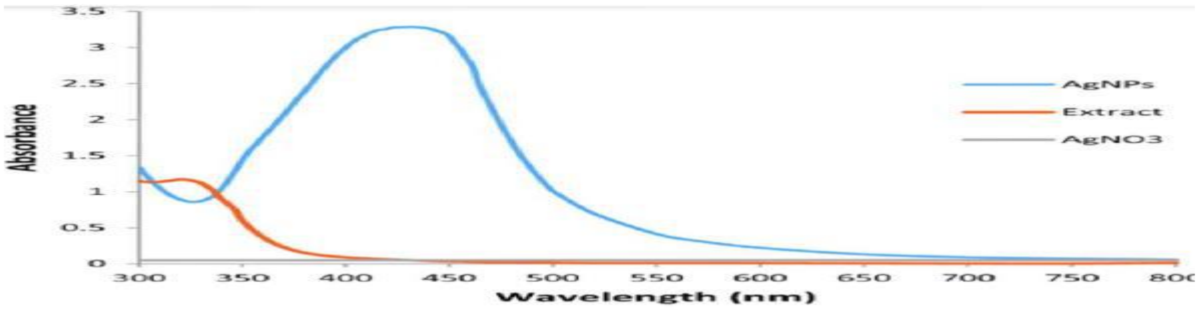

Figure 3. UV-Visible spectroscopy of $AgNO_3$ Soymida febrifuga plant extract and silver NPs of Soymida febrifuga plant.

Effect of Reaction Time:

The optimal time for the synthesis of SFAgNPs was examined through the UV-Vis spectra of the reaction mixture at various time intervals. As the reaction time increases, the redshift of the absorption peak designates an increase in the size of the NPs (Figure 2A). The increase in the intensity of the absorption peak over time is due to the increase in the number of absorbed metallic NPs (40,41). The synthesis of AgNPs from Solanum trilobatum extract was also studied by Vanaja et al., who observed a sharp narrow peak at 420 nm after 20 min of reaction indicating the synthesis of AgNPs, which was shifted to 440 nm after 20 min. With an increase of reaction time, the AgNPs production went on increasing, and the maximum absorption peak denoted the highest yield. The completion of the reaction occurred within 4h, which was also visualized by precipitate formation at the bottom (42,43).

Effect of Silver Nitrate Concentration:

The optimal concentration for the synthesis of SFAgNPs was found by varying concentrations of silver nitrate. The optimal concentration for NPs synthesis was found to be 1 mM (FigureT2B). Usually, by increasing the AgNO3 concentration, the fabrication of AgNPs is increased, and the color of the solution is enhanced because the accumulation of silver ions takes place, and larger NPs are attained (44,45). As the concentration of silver nitrate increases, the plasmon resonance (SPR) band becomes wider (46,47). Similarly, 1mM silver nitrate was found to be optimal for the synthesis of silver nanoparticles from Garcinia mangostana extract(15)(48)

SEM Investigation:

The SEM images of prepared SFAgNPs showed that these nanoparticles are spherical. Some small NPs aggregated into larger particles, which is due to the existence of secondary metabolites occurring in the Soymida febrifuga bark extract (Fig.4). The SEM figure showed a wide distribution of prepared NPs ranging from 10 to 130 nm in size.

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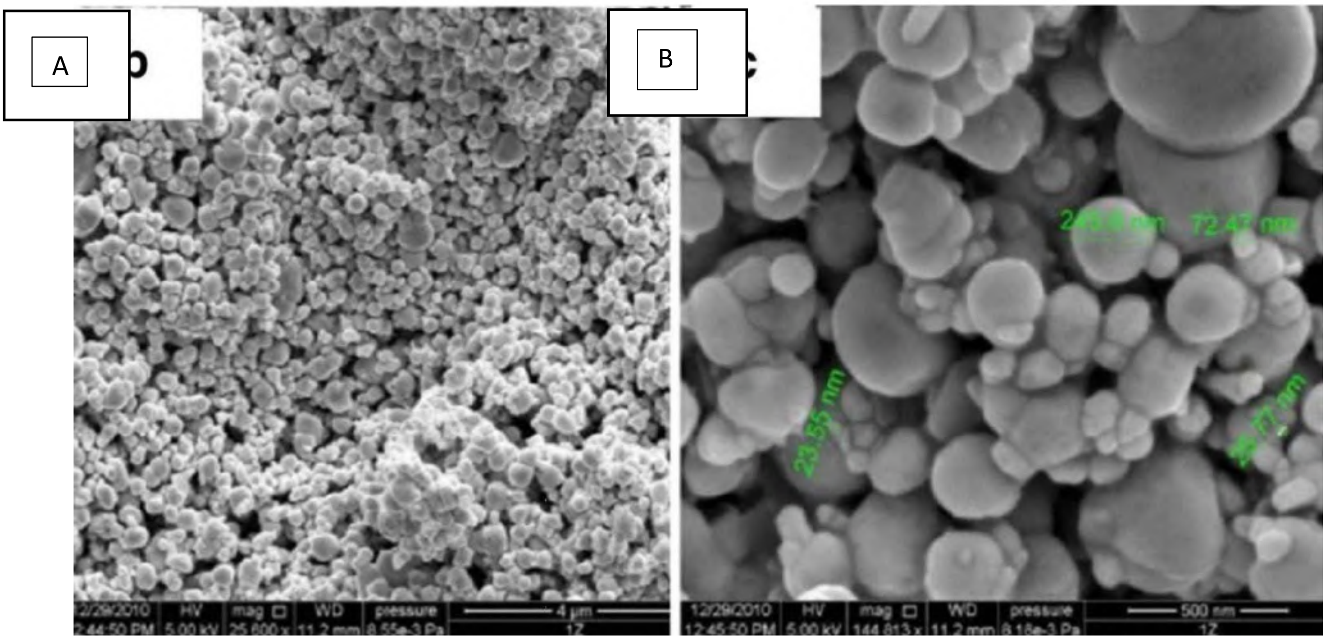

Figure 4. SEM pictures A and B of biosynthesized SFAgNPs.

FTIR Analysis

FTIR characterized the bark extract of Soymida febrifuga and the resultant biogenic SFAgNPs. The FTIR spectra for the bark extract and SFAgNPs are shown in FTIR graph. The characteristic absorbance bands for Soymida febrifuga and SFAgNPs can be seen at 1631cm−1 , 1588 cm−1 , 1384 cm−1 , 1400 cm−1 , 1126 cm−1 , 759 cm−1 at the wavelength range of 400–4000cm−1

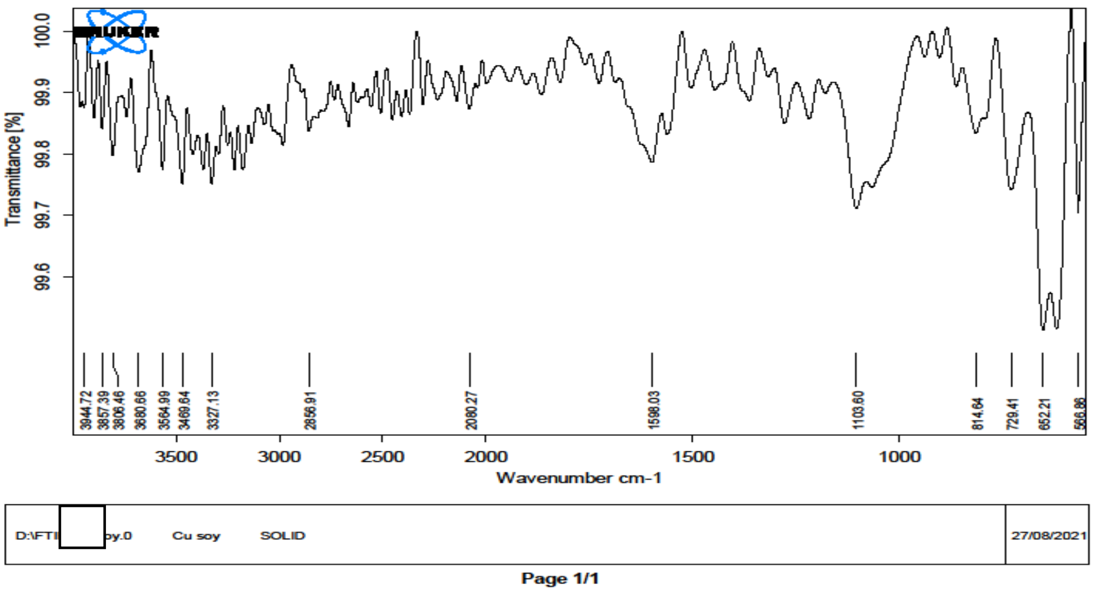

Figure 5. FTIR spectra of Silver Nanoparticles of Soymida Febrifuga bark

Which proved the presence of major functional groups of plant extract in the prepared NPs confirming capping and reduction of SFAgNPs with the plant extract.

Removal of Dyes by SFAgNPs:

The ultra-fast catalytic reduction of dye pollutants using biosynthesized AgNPs can be discussed based on surface adsorption behavior of dyes. Generally, the biological molecules or surfactants are used for capping of nanoparticles in chemical reduction methods, which makes an insulating layer around the nanoparticles and affect the diffusion of dye molecules to adsorb efficiently on surface of metal particles. However, the biomolecules can easily be separated by simple washings with water and thus does not restrict the adsorption of dye molecules on metal surfaces, which makes them efficient catalysts. AgNPs catalyzed reduction of pollutants can also be explained by electrochemical means, in which the AgNPs behave as an electron relay for oxidant and reductant

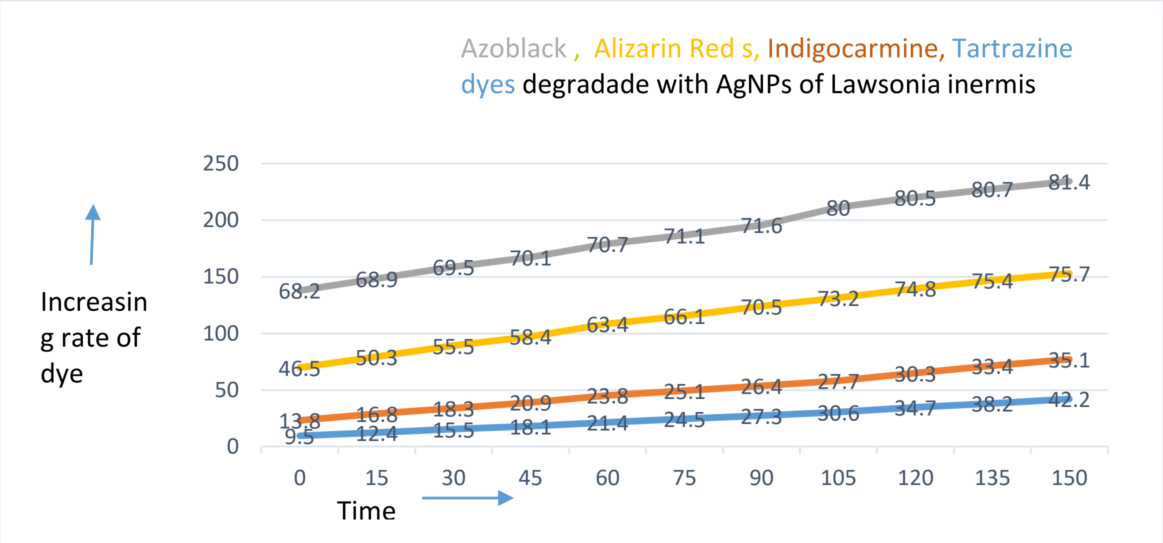

Figure 7: Degradation of Azoblack, Alizarine, Indigocarmine and Tartrazine dyes with AgNPs of Soymida Febrifuga (Mansrohini) plant with increasing time with photo catalytic activity.

4. CONCLUSIONS:

The green chemistry approach was employed for the rapid and effective synthesis of silver nanoparticles using Soymida febrifuga bark extract without any harmful side effects. These synthesized SFAgNPs were successfully optimized by UV-Vis spectroscopy by using different ratios of silver nitrate and bark extract, and reaction time. Phytochemical screening of the Soymida febrifuga bark extract was done to confirm which functional groups are present in the extract which was further confirmed by FTIR analysis when the detected function groups (Flavonoids, terpenoids, steroids, amides, alkaloids, and tannins) caused the reduction and stabilization of the synthesized NPs. The size and morphology of the SFAgNPs were examined by SEM confirming the spherical-shaped nanoparticles with size ranging from 20–25 nm. The synthesized AgNPs exhibited excellent role as wastewater disinfectant and dye degradation under the photocatalytic activity and it showed to be decreased by 60-80%, confirming its role in disinfecting wastewater.

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