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SILVER NANOPARTICLES FABRICATION USING MARINE PLANT (*MAYACA FLUVIATILIS*) RESOURCES

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Abstract: The synthesis, characterization and application of biologically synthesized nanomaterials have become an important branch of nanotechnology. A wide range of nanophasic and nanostructured particles are being fabricated globally with the aim of developing clean, nontoxic and eco-friendly technologies. In this paper, we report the synthesis of highly dispersed nanoparticles using a marine plant (*Mayaca fluviatilis*) extract as the reducing agent. Silver nanoparticles was investigated employing UV/Visible spectrophotometry, SEM (Scanning Electron Microscopy) and TGA (Thermal Analysis). *Mayaca fluviatilis* was found to exhibit strong potential for rapid reduction of silver ions. It was observed that there is no correlation always between the colour development and the increase in absorbance exhibited by the nanometal synthesised. The work adds to the confirmation of previous reports on biosynthesis of nanometals using a marine plant.

INTRODUCTION

Noble metal nanoparticles (NPs) are well known to have important applications in the fields of electronic, magnetic, optoelectronics, and information storage. It is now understood that the intrinsic properties of a noble metal NP are determined by its size, shape, composition, crystallinity, and structure (solid or hollow). Silver NPs, as a significant member of the noble metal NPs, are excellent substrates for surface enhanced Raman scattering (SERS) to probe single molecules, and are excellent as catalysts for accelerating some chemical reactions [1].

Nanoparticles are being viewed as fundamental building blocks of nanotechnology. The most important and distinct property of nanoparticles is that they exhibit larger surface area to volume ratio. The most effectively studied nanoparticles today are those made from noble metals, in particular Ag, Pt, Au and Pd. Metallic nanoparticles have tremendous applications in the area of catalysis, optoelectronics, diagnostic biological probes and display devices; silver nanoparticles play a significant role in the field of biology and medicine [1,2].

Nanocrystalline silver particles have found tremendous applications in the field of high sensitivity biomolecular detection and diagnostics, antimicrobials and therapeutics. However, there is still need for economic, commercially viable as well environmentally clean synthesis route to synthesize silver nanoparticles [2].

Synthesis using bio-organisms, especially plants that secrete the functional molecules for the reaction, is compatible with the green chemistry principles: the bio-organism is ecofriendly as are the reducing agent employed, and the capping agent in the reaction [1,3].

Biosynthesis of nanoparticles by plant extracts is currently under exploitation. The use of *Azadirachta indica* (Neem) [4], *Medicago sativa* (Alfalfa) [5], Aloe vera [6], *Emblica officinalis* [7], *Spinacia oleracea* (spinach) [8] and microorganisms [9,10] has already been reported. According to previous reports, the polyol components and the water-soluble heterocyclic components are mainly responsible for the reduction of silver ions and the stabilization of the nanoparticles, respectively [11].

A number of approaches are available for the synthesis of silver nanoparticles for example, reduction in solutions, chemical and photochemical reactions in reverse micelles, thermal decomposition of silver compounds, radiation assisted, electrochemical, sonochemical, microwave assisted process and recently via green chemistry route [2,12].

The use of environmentally benign materials like plant leaf extract [13], bacteria [14], fungi [15] and enzymes [16] for the synthesis of silver nanoparticles offers numerous benefits of eco-friendliness and compatibility for pharmaceutical and other biomedical applications as they do not use toxic chemicals for the synthesis protocol. Chemical synthesis methods lead to presence of some toxic chemical absorbed on the surface that may have adverse effect in the medical applications.

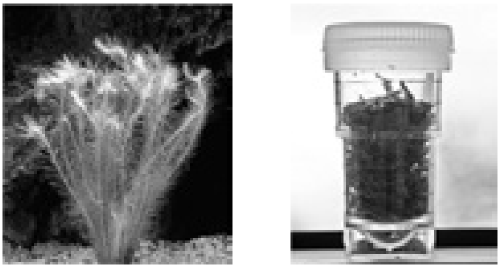
Green synthesis provides advancement over chemical and physical method as it is cost effective, environment friendly, easily scaled up for large scale synthesis and in this method there is no need to use high pressure, energy, temperature and toxic chemicals. [2].

Silver has long been recognized as having inhibitory effect on microbes present in medical and industrial process [17, 18]. The most important application of silver and silver nanoparticles is in medical industry such as topical ointments to prevent infection against burn and open wounds [19].

MATERIALS AND METHODS

Plant material and synthesis of silver nanoparticles

Mayaca fluviatilis was purchased a romanian shop. The marine plant was dried in the hot air oven at 105°C for 2 hours. And then were ground to a fine powder. After that, 10 mL of 10^{-3} silver nitrate was added to plant extract to make up a final solution which have stored over night at -4°C. A change in the color of solution was observed, the solution became yellow-brown.



a) b)

Figure 1a) Mayaca fluviatilis and .b) dried Mayaca fluviatilis

Apparatus

A M400 Carl Zeiss Jena UV spectrophotometer with a 1 nm slit width, 1 nm step size, 0.3 nm/s average scan rate, deuterium lamp, double beam, microprocessor and quartz cell was used to measure the aqueous solution absorbance and the molar absorption spectra for each sample at 22 ^{O}C.

The samples were examined using a Mettler 4000 TA, TG 50 thermal analyzer system at a rate of 10°C min^{-1} in a static air atmosphere; and a Perkin-Elmer thermoanalyzer TG S-2 and DTA 1700 at a rate of 10°C min^{-1}. Also, a TG (Du PontTGA) thermobalance is connected to a PC running Du Pont data processing software. The crucibles used were from Al_2O_3 and the diameter was from 70 µL. About 15 mg of sample were subjected to analysis in a temperature range 35-1000 C (10°C min^{-1}). Heating speed was 10 degrees 10°C/min. Liquid nitrogen's flow rate was set around 3 l/h.

The apparatus works in a low vacuum work. SEM analysis has been achieved with Quanta 200 Scanning Electron Microscope (SEM), which produces enlarged images of a variety of specimens, achieving magnifications of over 100000x providing high resolution imaging in a digital format. This important and widely used analytical tool provides exceptional depth of field, minimal specimen preparation, and the ability to combine the technique with X-ray microanalysis.

The Quanta 200 has 3 operating vacuum modes to deal with different types of sample:

- High Vacuum - the conventional operating mode associated with all scanning electron microscopes (pressure <1.3 Pa)
- Low Vacuum - when using uncoated, non-conductive samples (pressure 10-130 Pa)
- ESEM - when using moist samples dynamic experiments, hot/out gassing or dirty samples (pressure 130-2600 Pa)

Accessories: the Peltier cold stage - allows wetting/freezing of the sample using the ESEM mode pressure range.
Temperature range: -20 ÷ 80 °C

The operation of the SEM consists of applying a voltage between a conductive sample and filament, resulting in electron emission from the filament to the sample. This occurs in a vacuum environment ranging from 10^{-4} to 10^{-10} Torr. The electrons are guided to the sample by a series of electromagnetic lenses in the electron column. A schematic of a typical SEM is shown in figure 2.

Figure 2. SEM used for the measurements

Microstructure observations were performed with an environmental scanning electron microscope and equipped with analyzer and software for quantitative elemental analysis. For SEM analysis the powders were embedded in LR White resin. The surface of the resin blocks was ground to expose the powder; the blocks were then mounted on an aluminum stub and coated with carbon.

RESULTS AND DISCUSSION

Nanotechnology is a fast emerging discipline not only in physics and chemistry but also in the field of biology. In view of the tremendous applications of nanotechnology, there is a fillip among scientists to carry out research in this most vital discipline. Chemists are highly interested in synthesizing nanoparticles of different dimensions employing many of the precious metals. Already scientists have started exploiting the bio-based synthesis of nano-metals using leaf extracts and microorganisms (bacteria and fungi) [20].

The present study was conducted to screen the un-exploited plant sources in the development of silver nanoparticles. The marine plant *Mayaca fluviatilis* was selected and his rates of reduction of silver nitrate was investigated. It is well known that silver nanoparticles exhibit yellowish brown color in aqueous solution due to excitation of surface plasmon vibrations in silver nanoparticles [21]. As the marine plant which before was dried and then mixed in the aqueous solution of the silver ion complex, it started to change the color from watery to yellowish brown due to reduction of silver ion (Fig. 7); this a first evidence for the formation of silver nanoparticles.

It is generally recognized that UV–Vis spectroscopy could be used to examine size- and shape-controlled nanoparticles in aqueous suspensions [18]. Absorption spectra of silver nanoparticles formed in the reaction media has absorbance peak at 450 nm, broadening of peak indicated that the particles are polydispersed. The UV-VIS spectrum of the *Mayaca fluviatilis* extract is shown as an inset in Fig.3. The reduction of pure Ag^+ ions was monitored by measuring the UV-Vis spectrum. UV-Vis spectral analysis was done by using UV-VIS spectrophotometer M42. The strong resonance centered at 450 nm was clearly observed and increased in intensity with time. It might arise from the excitation of longitudinal plasmon vibrations in silver NPs in the solution. The stability of the silver nanoparticles can be seen more clearly by the figure, which shows the intensity of the absorbance at 450nm corresponding to the reaction time. It was observed that the solution containing the nanoparticles remained stable for more than six weeks, with no signs of aggregation or precipitate.

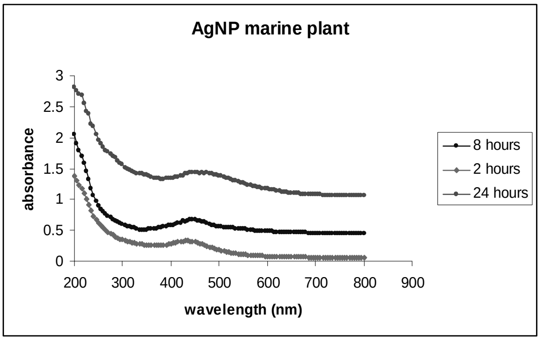


Fig.4 UV-Vis absorption spectrum of silver nanoparticles synthesized by treating 10 $^{-3}$ M aqueous AgNO3 solution with Mayaca fluviatilis after 2, 8 and 24 hours.

The biosynthesised silver nanostructure by employing marine plant was further demonstrated and confirmed by the characteristic peaks observed in the TGA image and the structural view under the scanning electron microscope.

In the fig. 5. is represented result of TGA analysis. It is observed for Ag the fact that the temperature point was at at 800°C.

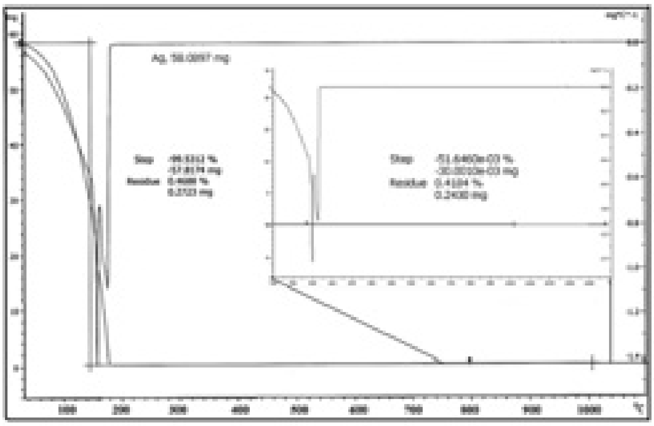


Fig. 5.The results of TGA analysis

The SEM image showing the high density silver nanoparticles synthesized by the *Mayaca fluviatilis* further confirmed the development of silver nanostructures.
The SEM image showing the high density silver nanoparticles synthesized by the marine plant further confirmed the development of silver nanostructures. The uniform size of the silver nanoparticles suggests that the particles on the cells and in the solution may have the same size. There was no obvious growth of the nanoparticles during the drying process at 60°C as a result of the well protection from the biomass.

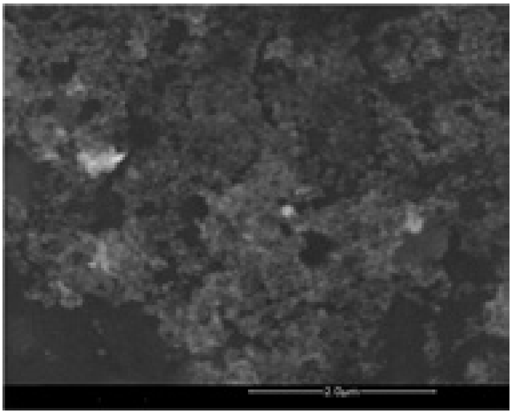


Fig.6 SEM micrograph of the silver nanoparticles

The most needed outcome of this work will be the development of value-added products from *Mayaca fluviatilis* for biomedical and nanotechnology based industries.

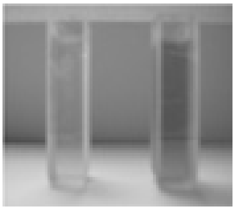


Fig. 7 left - solution of $AgNO_3$, right - solution of AgNP in marine plant (weak yellow-brown color)

CONCLUSION

In conclusion, the bio-reduction of aqueous Ag^+ ions by the fruit extract of the marine plant has been demonstrated. A green chemistry synthetic route has been used for silver nanoparticles synthesis. The reaction occurred at ambient temperature. Analytical techniques were applied to characterize the nanoparticles morphology. Silver nanoparticles have a number of applications from electronics and catalysis to biology, pharmaceutical and medical diagnosis and therapy.
This green chemistry approach toward the synthesis of silver nanoparticles has many advantages such as, ease with which the process can be scaled up, economic viability, etc. Applications of such eco-friendly nanoparticles in bactericidal, wound healing and other medical and electronic applications, makes this method potentially exciting for the large-scale synthesis of other inorganic materials (nanomaterials). Toxicity studies of silver nanoparticles on human pathogen opens a door for a new range of antibacterial agents.

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