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Switchgrass (*Panicum virgatum*) Extract Mediated Green Synthesis of Silver Nanoparticles

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ABSTRACT

A novel switchgrass (*Panicum virgatum*) extract mediated green process was demonstrated for the synthesis of silver nanoparticles from silver nitrate solution at ambient temperature. UV-visible spectroscopic analysis indicates the rapid reduction of silver (Ag^+) ions by swithgrass extract. The silver nanoparticles began to form at 15 min and the reduction reaction was completed within 2 hours. Synthesized silver nanoparticles were subjected to x-ray diffraction (XRD) for structural characterization, which confirms the FCC symmetry of silver nanoparticles with the lattice parameter of 4.0962 Å. The particle size of bio-synthesized silver nanoparticles was identified through transmission electron microscopic (TEM) analysis and found to be in the range of 20 - 40 nm.

Keywords: *Panicum virgatum*; Biosynthesis; Silver Nanoparticles

1. Introduction

Silver nanoparticles receive enormous scientific, technological, and commercial attention due to their unique size and shape dependent properties [1,2]. Extensive research has been devoted to explore the applications of silver nanoparticles in diversified fields including healthcare/ biomedical [3-5], sensors [6], spectroscopy [7] and catalysis [8]. One of the challenging tasks in the synthesis of nanostructured materials is the precise control of size and shape [9]. Especially, silver nanoparticles exhibit drastic variation in their physicochemical properties with the size, shape, and their conjugation with other organic/ biological substances [10-12]. The synthesis processes of silver nanoparticles play a major role in the control of their size and shape, thus wide range of physical, chemical, as well as biological methods have been established and reported [13-15]. Among them, biological processes that are based on bacteria, fungus, bio-derived chemicals, and plant extracts are extensively investigated due their eco-friendly protocol and better morphological control [16-18]. Using "green" methods in the synthesis of silver nanoparticles has increasingly become a topic of interests as conventional chemical methods are expensive and require the use of chemical compounds/organic solvents as reducing agents.

Recently, plant (leaf, flower, seed, tuber, and bark) extract mediated biological process for the synthesis of silver nanoparticles has been extensively explored and compared to other bio-inspired processes [19-26]. A range of plant extracts have been investigated for their ability to efficiently synthesize silver nanoparticles, and are mentioned as follows. Shankar *et al*., demonstrated a geranium (*Pelargonium graueolens*) leaf extract based biological process for the synthesis of silver nanoparticles [21]. Song *et al*., used persimmon (*Diopyros kaki*) leaf extract for the synthesis of bimetallic gold/silver nanoparticles [22]. Sathishkumar *et al*. has synthesised silver nanoparticles using *Cinnamon zeylanicum* bark extract and reported their bactericidal activity [23]. Ananda Babu *et al*. reported the synthesis of silver nanoparticles using *Calotropis procera* flower extract at room temperature [24]. In addition, we have also explored the synthesis of silver nanoparticles using soy (*Glycine max*) and curry (*Murraya Koengii*) leaf extracts [25,26]. Similarly, neem (*Azadirachta indica*) and mango (*Mangifera indica*) leaf extracts were effectively utilized for the synthesis of silver nanoparticles [27,28]. Apart from silver nanoparticles, plant extract mediated biological processes are also explored for the synthesis of gold and palladium nanoparticles [29,30]. Detailed literature work on the plant extract mediated biological synthesis of metal nanoparticles has been performed by Rai *et al*. and Iravani [31,32]. Recent accomplishments in the plant leaf extract mediated biological process include the impregnation of silver nanoparticles into carbon nanotubes, which

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indicates new opportunities for this process in the development of novel multifunctional materials [33,34].

Present research has prompted for further exploration in the use of plant extracts for the synthesis of silver nanoparticles from switchgrass extract. Switchgrass is a warm-season perennial plant that requires minimal agriculture inputs (including pesticides, energy, and fertilizer), with the ability to survive on marginal lands, providing economic and environmental advantages. Switchgrass has been widely used as fuel for generating energy and is currently used as feedstock for bio-ethanol production. Despite these developments in its many uses, there are currently no reports that show the bio-reduction mechanism of switchgrass extract for the synthesis of silver nanoparticles. This report outlines the use of switchgrass extract as the reducing agent in the reaction that converts silver ions into silver nanoparticles. Bioreduction mechanism of switchgrass extract for the synthesis of silver nanoparticles was investigated trough UV-visible, XRD, TEM, and XRD techniques.

2. Experimental

2.1. Preparation of Switchgrass Extract

The switchgrass extract was made using 20 g of fresh switchgrass, which was obtained from the Elora Research Station, University of Guelph, Ontario. A photograph of switchgrass is shown in **Figure 1**. Prior to extract preparation, the switchgrass was cleaned thoroughly using deionized water and then cut into small pieces. The switchgrass sample was then added into 125 mL of boiling deionized water, and left to boil for 3 minutes. The solution was then removed from the heat source and left to cool to ambient temperature (approximately 23˚C). Following this step, the extract was then filtered through a course sieve to remove any leaf matter and the resultant filtrate was then refrigerated.

2.2. Synthesis of Silver Nanoparticles

The silver nitrate ($AgNO_3$) used in this experiment was obtained from Sigma Aldrich. 3 mL of switchgrass extract was added to 60 mL of 10^{-3} M $AgNO_3$ solution and the reaction was left to take place at ambient conditions. The observed change in color from colorless to transparent yellow and finally to a dark brown with time, indicating the formation of silver nanoparticles. Reduction of the Ag^+ ions was monitored with respect to time using UV-visible spectral analysis. Once the reaction mixture had reached a dark brown color, it was then centrifuged in order to collect the silver nanoparticles. The nanoparticles were washed an additional two times using deionized water, and were then re-suspended in 95% ethanol (Fisher Scientific) prior to characterization.

Figure 1. Photograph of switchgrass.

2.3. Characterization

Optical absorbance of the synthesized silver nanoparticles was performed using a UV-visible spectrophotometer (Varian Cary 300 Bio) between the wavelengths of 300 and 700 nm at a resolution of 1 nm. The reaction mixture was first diluted 15 times with distilled water and used for UV-visible analysis. Transmission electron microscopy (TEM) was performed on the silver nanoparticles using a LEO model 912 AB instrument at the accelerating voltage of 100 k. A drop of the silver nanoparticle-ethanol dispersion was placed on a carbon coated copper grid, which allowed the ethanol to evaporate before analysis began. The phase purity and the crystalline structure of bio-systhesized silver nanoparticles were investigated through x-ray diffraction technique using a Rigaku Mul-tiflex x-ray powder diffractometer employing CuKα radiation. The silver nanoparticle dispersion was placed on a glass slide and the solution (ethanol) was allowed to evaporate such that a thin film of silver nanoparticles remained. This thin silver film was subjected to x-ray diffraction operating between 10˚ and 80˚, with a scanning rate of 2˚ per minute. The average crystallite size of the silver nanoparticles was calculated using a line broadening profile of (111) peak at 38˚ and Sherrer's formula as follows,

$$d = 0.9\,(\lambda)/\beta\,\mathrm{Cos}\,\theta$$

where λ is the wavelength (1.5418 Å), β is the full width half maximum (FWHM) of corresponding peek, and θ is the angle of the diffraction peek.

3. Results and Discussion

Figure 2 shows the color change of reaction mixture (silver nitrate solution and switchgrass extract) with respect to time. Color change can be observed at 15 minutes from colorless to faint yellow, indicating the formation of silver nanoparticles. As time elapsed, the yellow colored solution eventually became dark brown at 120 minutes, which is due to the increasing concentration of silver nanoparticles as well as the particles' growth in size. There

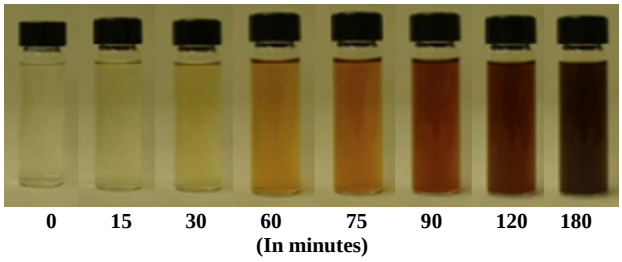
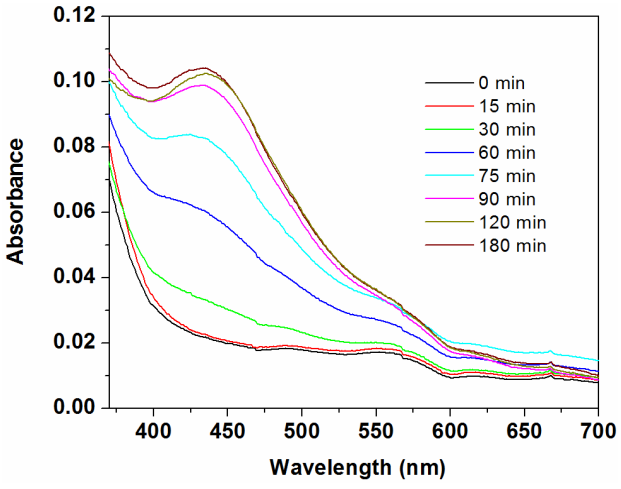


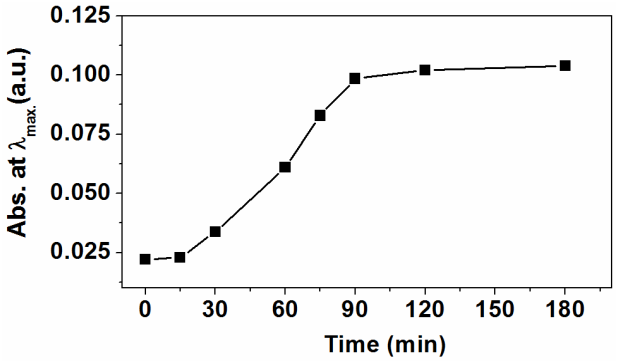
Figure 2. Photograph of reaction mixture (switchgrass extract and silver nitrate solution) as a function of time.

is no significant change beyond 180 minutes, therefore indicating the completion of the reduction reaction. This was further confirmed by UV-vis spectroscopic analysis. This physical appearance of the reaction mixture turning from yellow to brown is due to the surface plasmon resonance (SPR) of the silver nanoparticles, which is considered to be the primary signature of nanoparticle formation. UV-vis spectroscopy is a versatile technique to understand the bioreduction mechanism of silver ions into silver nanoparticles by switchgrass extract. The UV-vis spectra of the reaction mixture recorded as a function of time, is are shown in **Figure 3(a)**. An observed peak at 435 nm is assigned to the surface plasmon resonance band (longitudinal vibration) of the silver nanoparticles, which is comparable with the literature values and exhibits continuous rise in intensity without any change in the peak position as a function of time. During 15 - 60 minutes intervals the absorption peak was weak and broad, which indicates the smaller size of silver nanoparticles. Nucleation occurs between 60 - 90 minutes, which appeared as strong a absorption peak, as shown in **Figure 3(a)**. **Figure 3(b)** shows the absorbance at λ_{max} (*i.e.* at 435 nm) as a function of time. From **Figure 3(b)** it is indentified that the reduction of silver ions to silver nanoparticles occurs quite rapidly, as more than 90% of the bioreduction reaction completes within 90 minutes. This is faster than earlier studies of the synthesis of silver nanoparticles using biological sources.

The crystalline structure of the bio-syntheized silver nanoparticles was investigated by XRD analysis and the obtained x-ray diffraction pattern is shown in **Figure 4**. The obtained diffraction peaks at 38˚, 44˚, 64˚ and 77˚ are respectively assigned to (111), (200), (311) and (222) plans, which indicates that the synthesized silver nanoparticles are crystallized in face centered cubic (fcc) symmetry. No additional diffraction peaks were observed other than the characteristic peak of the silver structure that reflects the purity of synthesized silver nanoparticles. The lattice parameter (A) of the bio-synthesized silver nanoparticles was calculated from the diffraction data and was found to be A = 4.0962 Å, which is comparable with the JCPDS value. The calculated crystallite size has been found to be ~10 nm, which is comparable with the particle size as obtained from TEM analysis.



(a)



(b)

Figure 3. (a) UV-vis absorption spectra of reaction mixture (switchgrass and silver nitrate) and (b) Absorbance at λ_{max} (*i.e.*, at 435 nm) as a function of time.

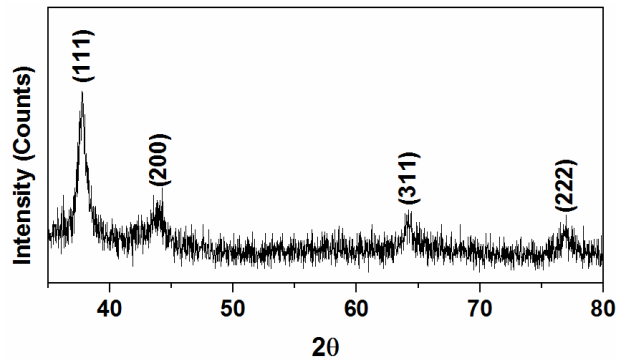


Figure 4. XRD pattern of silver nanoparticles synthesized using switchgrass extract.

The microscopic structure of the switchgrass extract mediated bio-synthesized silver nanoparticles was investigated by TEM analysis. The obtained TEM images are shown in **Figure 5**. TEM images confirm the formation of silver nanoparticles with the size range between 20 and 40 nm. In addition, the TEM images show the shape of the nanoparticles are highly diversified, which includes

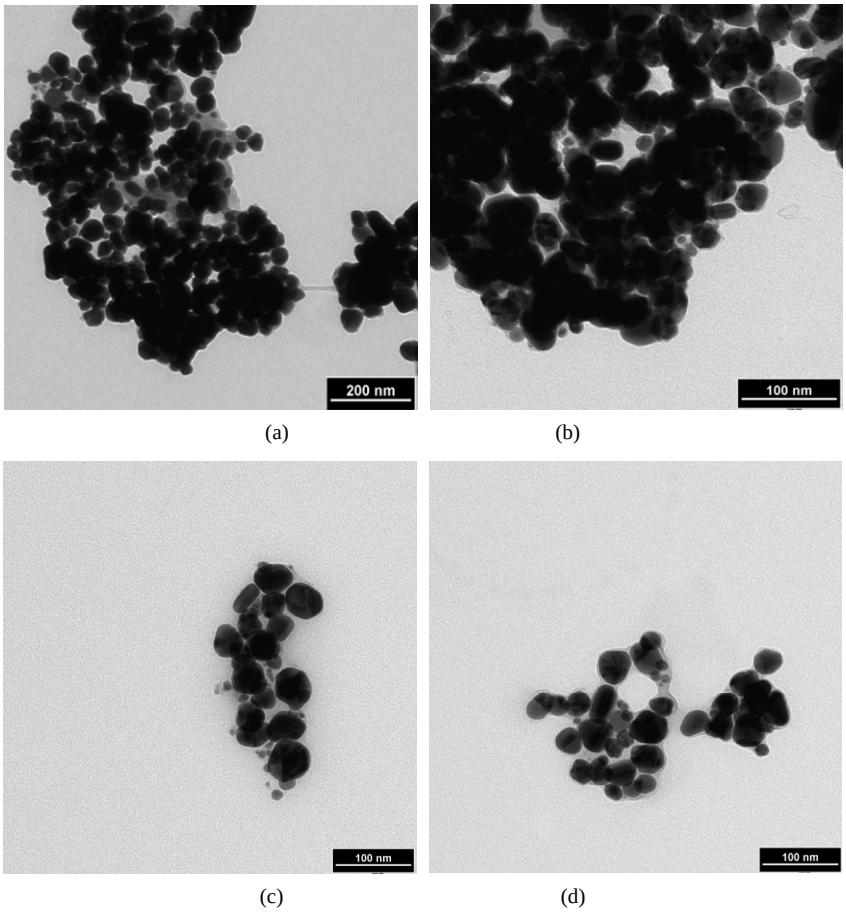


Figure 5. (a)-(d) TEM images of silver nanoparticles synthesized using switchgrass extract.

spherical, rod-like, triangular, pentagonal, and hexagonal. It was found that the synthesized silver nanoparticles have the tendency to aggregate and form the agglomerations.

The agglomerated silver nanoparticles assemble together without much physical contact. Thus they can be separated by physical agitation for the further utilization.

4. Conclusion

Silver nanoparticles were successfully synthesized using switchgrass extract used at room temperature. Synthesis of silver nanoparticles through this process was fairly rapid, with 90% of silver ion reduction completed within 90 minutes. TEM analysis confirms that the synthesized silver nanoparticles exist between 20 and 40 nm and exhibit the tendency to aggregate. XRD analysis indicates the formation of phase pure silver nanoparticles with FCC symmetry. The calculated average crystallite size is found to be of 10 nm, which is consistent with TEM analysis. The fundamental understanding of switchgrass mediated biological process for the synthesis of silver nanoparticles will allow the expansion of this process for the synthesis of gold and palladium nanoparticles and their applications.

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