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# Green synthesis of silver nanoparticle for the selective and sensitive colorimetric detection of mercury (II) ion

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ABSTRACT

An ecofriendly and zero cost approach has been developed for the photoinduced synthesis of more stable AgNPs using an aqueous extract of *Murraya koenigii* (AEM) as a reducing and stabilizing agent. The exposed reaction mixture of AEM and $AgNO_3$ to sunlight turned dark brown which primarily confirmed the biosynthesis of AgNPs. The biosynthesis was monitored by UV–vis spectroscopy which exhibited a sharp SPR band at 430 nm after 30 min of sunlight exposure. The optimum conditions for biosynthesis of AgNPs were 30 min of sunlight exposure, 2.0% (v/v) of AEM inoculuam dose and 4.0 mM $AgNO_3$ concentration. TEM analysis confirmed the presence of spherical AgNPs with average size 8.6 nm. The crystalline nature of the AgNPs was confirmed by XRD analysis where the Bragg's diffraction pattern at (111), (200), (220) and (311) corresponded to face centered cubic crystal lattice of metallic silver. The surface texture was analyzed by AFM analysis where the average roughness of the synthesized AgNPs was found 1.8 nm. FTIR analysis was recorded between 4000 and 400 $cm^{-1}$ which confirmed the involvement of various functional groups in the synthesis of AgNPs. On the basis of the linear relationship between SPR band intensity and different concentration of $Hg^{2+}$, the synthesized AgNPs can be used for colorimetric detection of $Hg^{2+}$ with a linear range from 50 nm to 500 μM. Based on experimental findings, an oxidation-reduction mechanism between AgNPs and $Hg^{2+}$ was also proposed.



## 1. Introduction

Nanobiotechnology is an emerging field of science and technology for the development, improvement, and utility of nanostructures [1]. Since last two decades the green synthesis of silver nanoparticles (AgNPs) has received a considerable attention of the researchers due to growing need in several fields; such as, catalysis [2], biosensing [3], antibacterial [4], antioxidant [5] antiviral [6] and anticancer [7], wound healing [8], medicine [9]. The principles of green chemistry have played a prominent role in nanobiotechnology as it employed the involvement of green and eco-friendly route using algae [10], fungi [11] and plants [3] for the synthesis of silver nanoparticles. Currently, green synthesis is most preferred as it avoids the sophisticated instrumentations, technical expertise and excessive use of toxic chemicals hazardous to the environment [12–18].

At present, plant extracts mediated green synthesis is more advantageous over other biological systems as it eliminates the need of culture, aseptic condition and maintenance [2–3]. In addition to this, the plant extract mediated synthesis is user-friendly, economical and less biohazard process. It contains various phytochemicals such as terpenoids, flavonoids, phenol derivatives and plant enzymes like hydrogenases, and reductases which act as both reducing and capping agent which reduce the metal salts and deters the aggregation of the nanoparticles [4–5]. Hence; currently, the plant extracts are being used extensively as a reducing agent for the synthesis of AgNPs [19]. Recently, several plants like *Rosmarinus officinalis* [20], *Coffea arabica* [21], *Crataegus douglasii* [22], *Skimmia laureola* [23], etc. have been reported for the green synthesis of AgNPs (Table 1).

The photoinduced green synthesis of AgNPs using plant extract is proved to be more economic efficient and eco-friendly where the visible light increases rate of biosynthesis. There are several articles which have been published for the biosynthesis of AgNPs using sunlight induced route. In our previous study, we have reported the photoinduced synthesis of silver nanoparticles using an aqueous extract of *Erigeron bonariensis* [2], *Croton bonplandianum* [3], *Euphorbia hirta* [4], *Polyalthia longifolia* [5], *Salvinia molesta* [24] and *Xanthium strumarium* [25] through sunlight induced route. The plant *Murraya koenigii* belongs to family Rutaceae, commonly called as curry leaf. *Murraya koenigii* is a native of, Sri Lanka, India, and other South Asian countries which is used traditionally as antiemetic, antidiarrhoeal, and blood purifier. Phytochemical analysis of leaves revealed the presence of carbohydrate,

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**Table 1**
Table showing the list of different plants for the green synthesis of silver nanoparticles.

| Plant | Part used | Extract type | UV–vis | Shape | Size | *Activity* | Stability | Reference |
|---|---|---|---|---|---|---|---|---|
| *Murraya koenigii* | Leaves | Aqueous | 425 | Spherical | 8.6 nm | $Hg^{2+}$ detection | 4 month | Current Study |
| *Erigeron bonariensis* | Leaves | Aqueous | 435 | Spherical | 13 nm | Catalytic | 7 days | [2] |
| *Croton bonplandianum* | Leaves | Aqueous | 428 nm | Spherical | 19.4 nm | $Fe^{3+}$ detection, antibacterial and Antioxidant | 9 month | [3] |
| *Euphorbia hirta* | Leaves | Aqueous | 425 nm | Spherical | 15.4 nm | Antibacterial and hydrogen peroxide detection | – | [4] |
| *Polyalthia longifolia* | Leaves | Aqueous | 450 nm | irregular | 13.4 nm | Antioxidant | 7 days | [5] |
| *Aegle marmelos* | Leaves | Aqueous | 422 nm | Spherical | 60 nm | – | | [13] |
| *Dalbergia spinosa* | Leaves | Aqueous | 439 nm | Spherical | 18 ± 4 nm. | Antibacterial and Catalytic | – | [16] |
| *Boerhaavia diffusa* | Leaves | Aqueous | 418 nm | Spherical | 25 | Antibacterial | | [17] |
| *Platanus orientalis* | Leaves | Aqueous | 430 nm | cubical | 15–500 nm | – | | [18] |
| *Diopyros kaki* | Leaves | Aqueous | 430 nm | cubical | 15–500 nm | – | | [18] |
| *Ginko biloba* | Leaves | Aqueous | 430 nm | cubical | 15–500 nm | – | | [18] |
| *Magnolia kobus* | Leaves | Aqueous | 430 nm | cubical | 15–500 nm | – | | [18] |
| *Ficus benghalensis* | Leaves | Aqueous | 410 nm | Spherical | 16 nm | Antibacterial | | [19] |
| *Rosmarinus officinalis* | Leaves | Aqueous | 450 nm | Spherical | 29 nm | Antibacterial | – | [20] |
| *Coffea arabica* | Seed | Hydro-alcoholic | 459 nm | Spherical | 10–40 nm | Antibacterial | – | [21] |
| *Crataegus douglasii* | Fruit | Aqueous | 425 nm | Spherical | 29.28 nm | Antibacterial | – | [22] |
| *Skimmia laureola* | Leaves | Aqueous | 460 nm | Spherical and Hexagonal | 38 nm | Antibacterial | – | [23] |
| *Salvinia molesta* | Leaves | Aqueous | 425 nm | Spherical | 12.46 nm | Antibacterial | 7 days | [24] |
| *Xanthium strumarium* | Leaves | Aqueous | 436 nm | Spherical | 18 nm | Antibacterial and antileishmanial | 2 days | [25] |
| *Artocarpus heterophyllus* | Seed | Aqueous | 410 | Irregular | 10.78 nm | Antibacterial | | [30] |
| *Mimusops elengi* | Leaves | Aqueous | 434 nm | Spherical | 55–83 nm | Antibacterial | 30 days | [32] |
| *Jatropha curcas* | Seed | Aqueous | 425 nm | Spherical | 20–30 nm | – | | [35] |
| *Citrus lemon* | Juice | Aqueous | | Spherical | <50 nm | – | – | [39] |
| *Morinda citrifolia* | Root | Aqueous | 540 nm | Triangular and spherical | 12–38 nm | – | – | [42] |

tannin, alkaloid, steroid, triterpenoid, flavonoids, saponins, sugars, and protein [26,27].

The main objective of the present study is photoinduced, one pot and green synthesis of stable AgNPs using an aqueous leaf extract of *M. koenigii*. It was also tried to avoid the utilization of any toxic chemical, technical expertise and sophisticated instrumentation in the synthesis of AgNPs which might make it eco-friendly, economical and nonhazardous. Thus parameters affecting the synthesis of the AgNPs would also be optimized and the optimum AgNPs thus obtained would be applied for the investigation of sensing potential towards of different metal ions.

## 2. Materials and Method

In the current study, silver nitrate ($AgNO_3$), the only chemical used for the synthesis of AgNPs was of analytical grade having high purity and sourced from Merck, India. The standard stock solution (1 mM) of metal ions ($Fe^{3+}$, $Fe^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Co^{2+}$, $Al^{3+}$, $As^{3+}$, $As^{5+}$, $Cu^{2+}$, $Hg^{2+}$, $Cr^{6+}$) were prepared with ultrapure water from the respective metal salts ($FeCl_3$, $Cl_2Fe{\cdot}4H_2O$, $Pb(NO_3)_2$, $Cd(NO_3)_2{\cdot}4H2O$, $Co(NO_3)_26H_2O$, $Al(NO_3)_3$, $As_2O_3$, $Na_2HAsO_47H_2O$, $CuCl_22H_2O$, $Hg(NO_3)_2{\cdot}H_2O$, $K_2Cr_2O_7$. Fresh leaves of *M. koenigii* were collected from campus area of Indian Institute of Technology (Banaras Hindu University), Varanasi, India and were further processed in the lab to prepare leaf extract.

### 2.1. Preparation of Leaf Extract

The aqueous leaf extract of *M. koenigii* was made by washing the fresh leaves several times with deionized water to remove dust and other adhering impurities. After that, the leaves were air dried under shade to eradicate the moisture completely. The dried leaves were cut into fine pieces, and 25 g of it was boiled for 10 min in 100 mL of deionized water. After that, the aqueous extract of *M. koenigii* (AEM) was collected and filtered through Whatman filter paper No. 1. The prepared AEM was stored as a stock solution at 4 °C and used within 3 days (Fig. S1).

### 2.2. Biosynthesis of AgNPs

For the biosynthesis of AgNPs 1% (v/v) of AEM inoculum dose was added into 100 mL of 1 mM $AgNO_3$ solution and exposed to bright sunlight. The pH of the reaction mixture was neutral. The temperature of the ambient environment in bright sunlight and solar intensity of incident sunlight radiation were 29 °C and 63,600 lx. The color of the reaction mixture exposed to bright sunlight changed from colorless to reddish-brown instantaneously. This change in color confirmed the synthesis of AgNPs. The synthesis of AgNPs was regularly monitored using UV–visible spectroscopy. For the comparison purpose, the same experiment was also performed in dark condition by keeping it in a black colored closed vessel where the temperature of the dark condition and light intensities were 24 °C and 0 lx respectively. The reaction mixture kept in the dark did not exhibit any sharp SPR band as well as a significant change in color up to 6 h which clearly indicated the photo catalytic action of sunlight on synthesis of AgNPs. Therefore, further all the AgNPs synthesis experiments were performed in bright sunlight to optimize the other process variables using one factor at a time approach. The process variables like duration of sunlight exposure, AEM inoculum dose, and $AgNO_3$ concentration were screened for optimization purpose in the range from 0 to 30 min, 1.0%–6.0% (v/v) and from 1.0 mM to 6.0 mM respectively. After the completion of reaction at these optimized conditions the synthesized AgNPs were purified by centrifuging at 15,000 rpm for 15 min and subsequently re-dispersed in deionized water to eliminate the water soluble biological molecules and other secondary metabolites. This process was repeated four times and after vacuum drying the final mass of AgNPs was collected.

### 2.3. Characterization of AgNPs.

The optical property of AgNPs was studied UV–visible spectrophotometer (Evolution 201, Thermo Scientific) in the range of 300 to 800 nm. The involvement of several functional groups in the synthesis of AgNPs was investigated through Fourier transform infrared spectrophotometer (Perkin Elmer Spectrum 100) the range of 4000–400 $cm^{-1}$. The crystalline nature of AgNPs was determined using X-ray