An efficient and blistering reduction of 4-nitrophenol by green synthesized silver nanoparticles

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Abstract

The present work describes a clean, green and cost efficient approach for the synthesis of biogenic silver nanoparticles from the *Psidium guajava* leaf extract. The UV–Visible spectrum shows a sharp peak at 413 nm revealing the formation of silver nanoparticles (Ag NPs). The optical and morphological characterization confirms the formation of stable and mono disperse biogenic silver nanoparticles having average diameter in range of 20–30 nm. FTIR study confirms that the strong capping and reduction potential *Psidium guajava* leaf extract for the synthesis of Ag NPs. The synthesized Ag NPs shows the prodigious potential for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) within 8 min (ultra-high speed) with rate constant 0.159 min^{-1} . Kinetic study elucidate that the catalytic reduction follows the pseudo first order with R^2 value of 0.975.

Keywords Silver NPs · *Psidium guajava* · Catalysis · 4-Nitrophenol · Green synthesis

1 Introduction

In the modern era, the water is getting depleted by number of pollutants present in the waste effluents from the industries. It is necessary to remove these pollutants from the waste water on the account of their toxicity. The nitro group containing pollutants are of major concern as they are difficult to reduce because of their toxic behaviour [1–3]. Compounds like 4-nitro phenol (4-NP) are not only toxic but also anthropogenic and inhibitory in nature so their reduction is an issue of major importance. 4-nitrophenol is a phenolic compound, constitute one nitro group present on the benzene ring diagonally to the hydroxyl group. 4-NP cause eyes irritation and inflammation. It interacts with blood and forms methaemoglobin which results in forming methemoglobinemia; that causes cyanosis, confusion and unconsciousness. When ingested, it causes abdominal pain and vomiting. Moreover, 4-NP and its by-products are used for the further synthesis of

herbicides, insecticides and pesticides that causes threat to environment as well as to human beings [4, 5].

In the recent decades, with the increasing scope of nanotechnology the borohydride reduction of these nitro group compounds (4-nitrophenol) into useful and harmless compound (4-Aminophenol) by metal nanoparticles has been seeking attention due to the easy availability of the reaction conditions [6, 7]. Metal nanoparticles (NPs) because of their unique properties like large surface area to volume ratio, large surface energies as compared to their bulk counterparts; has numerous applications in biological, electrochemical and medical fields [8–10]. There are various metal nanoparticles were used for the reduction of these nitro derivatives. Among all the metal NPs, silver (Ag) NPs are of substantial interest as of its ability to tune plasmon resonance at any wavelength in visible spectrum region and it acts as good catalyst under normal conditions and ambient temperatures. Ag NPs have numerous applications like in catalysis [11], anti-microbial and in medicinal field [12]. There is number of methodologies

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to synthesize silver nanoparticles, such as thermal decomposition [13], microwave assisted [14], electrochemical [15] and green chemistry [8]. Due to the use of many chemicals in synthesis processes, the manufacturing process would be costly and it would cause toxicity. Therefore, an ecofriendly and cheapest method is gaining importance now a day. Biosynthetic methodology, using plant extract or microorganisms is usually more preferred over the chemical synthetic procedures and physical methods. Microorganisms such as bacteria, yeast or fungi can be used in synthesizing metal nanoparticles. Plant extract's constituent acts as reducing agents and stabilizing agents to form the metal NPs. Some of the plants like *Pelargonium graveolens* [16], *Azadirachta indica* [17], *Lemongrass* [18], *Cinnamomum Camphora* [19], *Emblica officinalis* [20], *Carica papaya* [21–27], *Oscium sanctum* [7] have the ability to reduce AgNO_3 to silver NPs.

In the present work, we adopted the one step, cost effective and eco-friendly method to synthesize the silver nanoparticles from the *Psidium guajava* (guava) leave extract. The synthesized silver nanoparticles were employed for the catalytic reduction of 4-NP into 4-AP. Also, the 4-AP has many useful pharmaceutical applications such as synthesis of paracetamol. Thus, this approach demonstrates the non-toxic, one pot innovative and green approach for the synthesis of NPs and their further use in the environment.

2 Materials and methodology

2.1 Materials

The *Psidium guajava* leaves are collected from the nearby garden in Fatehgarh Sahib. Silver nitrate salt was purchased from Sigma Aldrich. The other chemicals 4-NP and Sodium Borohydride (NaBH_4) were purchased from Merck, Germany for the further process. All these chemicals are of analytical grade and used without any purification. Double distilled water is used for aqueous solution. Whatman no. 1 filter paper is used for filtration.

2.2 Preparation of extract

The collected *Psidium guajava* leaves were washed with DI water and sun dried to eliminate water. Then the leaves were cut down into small fine piece. The 4 g leaves were weighed and boiled in 100 ml DI water. After 1 h lightish green yellow solution formed and separated from the particulate matter by using Whatman filter paper No: 1. The obtained solution was stored at 4 °C.

2.3 Synthesis of silver nanoparticles

Firstly, solution of AgNO_3 is prepared by adding 0.016 g of 10^{-2} M AgNO_3 in 100 ml of DI water. After that the 1 ml of the prepared extract solution was added drop wise to the 50 ml of AgNO_3 solution with continuous mild stirring. After sometime the colour of the solution starts to change from lightish green yellow to reddish brown indicating the formation of silver nanoparticles (Ag NPs).

2.4 Catalytic activity

To check the catalytic activity of synthesized Ag NPs, the reduction of 4-nitrophenol was carried out in the quartz cuvette in the presence of the sodium borohydride solution. In the cuvette 2.7 ml DI water taken. Then, the 30 μl of (10^{-2} M) 4-nitrophenol was mixed with water, and subsequently 200 μl of (10^{-1} M) NaBH_4 was added. Once all the solutions get mixed, then 10 μl of Ag NPs (catalyst) were added. Afterwards, The catalytic reaction was monitored by UV–Visible spectrophotometer with different time intervals. With the passage of time, yellow color solution turned into colorless solution indicating the reduction of 4-NP into 4-AP.

3 Results and discussion

3.1 UV–visible analysis

1 ml of prepared extract was added in the AgNO_3 solution for the reduction of Ag^+ into Ag^0 . The reaction was monitored spectrophotometrically on UV–vis spectrometer (model no. UV-2600, SHIMADZU, Japan). The change of color from the light greenish yellow into reddish brown color was observed, due to the surface plasmon excitations in the metal atoms. The formation of Ag NPs was confirmed by surface plasmon resonance phenomenon. The λ_{max} values for the biosynthesized Ag NPs were reported in between 400 and 500 nm that is a visible range. Figure 1 shows the Ag NPs synthesized by 1 ml extract volume. The particles synthesized by 1 ml extract gives sharp and strong absorption band at λ_{max} 413 nm.

3.2 Zetasizer analysis

The average diameter and particle size distribution (PSD) is determined by particle size analyzer (Malvern-ZEN-1690) that is based on laser diffraction technique. The average diameter of the biosynthesized Ag NPs was

Fig. 1 UV-visible spectrum of Ag NPs (black line) and *Psidium guajava* leaf extract (red line). The sharp band at 413 nm indicates the formation of Ag NPs

Fig. 2 DLS graph shows the particle size distribution of Ag NPs

estimated to be 50.90 with corresponding PDI value of 0.405 as depicted in Fig. 2.

3.3 FTIR analysis

The FTIR spectra of the Ag NPs exhibit the strong bands at 3728 cm^{-1} (O-H), 2915 cm^{-1} (C-H), 1691 cm^{-1} (C=O), 1531 cm^{-1} (C=C), 1039 cm^{-1} (C-O) and 784 and 676 cm^{-1} as shown in Fig. 3a. These functional groups (phenols, flavonoids, proteins) originated from *Psidium guajava* extract which can be observed in Fig. 3b. Thus, by comparing Fig. 3a, b, it was suggested that the these phytochemicals (present in extract) were responsible for the reduction and capping of Ag NPs [22–25]. Additionally, the capping capability of phytochemicals were also observed in HR-TEM micrographs (Fig. 5). The formation of the silver nanoparticles confirmed by the characteristics peak at 676 and 784 cm^{-1} due to the formation of bond between Ag and the O-atoms of the phytochemicals. All these values were in agreement with the already reported study [26, 27].

3.4 XRD analysis

The crystal structure and phase purity of synthesized Ag NPs was investigated by XRD study performed on X-ray diffractometer (model no. DY 3190, PANalytical XPERT-PRO, Japan). The XRD spectra showed the diffraction peaks at 37.9° , 44.1° , 64.4° , 77.5° corresponding diffraction planes (111), (200), (220) and (311) respectively. Therefore, the XRD analysis confirms the cubic crystal structure of Ag nanoparticles according to JCPDS Card No. 04–0783 (Fig. 4).

Fig. 3 FTIR spectra of **a** synthesized Ag NPs and **b** *Psidium guajava* extract

Fig. 4 XRD spectra of synthesized Ag NPs

3.5 HR-tem

The structural and elemental analysis of Ag NPs was employed by high resolution transmission electron microscopy (HR-TEM) and presented in Fig. 5. The observed average diameter from the HR-TEM analysis was in range of 20–30 nm with narrow particle size distribution. Also, the strong capping potential of phytochemicals present in *Psidium guajava* extract can be easily observed (small circles around the particles) in HR-TEM micrographs.

3.6 Catalytic reduction studies

The catalytic activity of synthesized silver nanoparticles was checked by reducing 4-NP in the presence of sodium borohydride. 4-nitrophenol is highly toxic and due to

the presence of electron withdrawing nitro group so it is difficult to remove this by simple oxidation and hydrolysis methods. The kinetics of the reduction process was studied spectrophotometrically as shown in the Fig. 6a. At $t=0$ min, the UV spectra as characterized by sharp absorption band at 400 nm indicating the formation of the nitrophenolate ion. Addition of biosynthesized Ag NPs will result in the rapid decline of the absorption intensity at 400 nm which is accompanied by the formation of wider band at 298 nm owing to the formation of 4-aminophenol. The color of the solution turns from bright yellow to colourless within 8 min, which signifies the efficient catalytic potential of synthesized Ag NPs and the importance of this study as well. The kinetic study confirms the catalytic reduction follows pseudo first order with rate constant 0.1579 min^{-1} as shown in Fig. 6b. Moreover, the reduction of 4-NP without Ag NPs is not possible, due to high activation energy barrier [28, 29]. Additionally, to validate the efficacy of present study, a comparison of previous studies was investigated as described in Table 1. It was observed that many studies used complex, expensive and harmful process to synthesize silver nanoparticles and their composites for reduction of 4-NP. Also, they require more time for complete reduction of 4-NP then the present study. Thus, this study provides many advantages such as adaptability of eco-friendly, inexpensive and simple process for the synthesis of Ag NPs, which have remarkable potential for the complete reduction of 4-NP with ultra-high speed (8 min).

Fig. 5 TEM images Ag NP's at **a** 50 nm and **b** 100 nm scale bar

Fig. 6 Schematic shows the **a** UV-Visible spectrum showing catalytic reduction of 4-Nitrophenol (400 nm) to 4-Aminophenol (298 nm) by 10 µL of Ag NPs in the presence of NaBH₄ at room temperature (Inset: chemical structure of 4-NP) and **b** kinetic study of catalytic reduction

Table 1 Performance comparison of Ag NPs based catalysts for the reduction of 4-nitrophenol to 4-aminophenol

Catalyst	Synthesis method	Catalyst loading	Reaction time	References
Ag NPs	Biodegradable amphiphilic copolymers	30 µL	12 min	[28]
Ag-P(NIPAM-co-AAm)	Precipitation polymerization	37.18 mg	25 min	[30]
Au, Ag NPs	Photochemical green	20 mg	45 min	[31]
Ag NPs by kollicoat	Chemical	50 mg	60 min	[32]
Biogenic Ag NPs	Green	10 µL	8 min	Present study

4 Conclusions

In conclusion, present study demonstrates a innovative and effective, one step method for the synthesis of the silver nanoparticles using the *Psidium guajava* leaves, that provides a greener route for the synthesis process. Spectroscopic and electronic microscopic studies confirmed the optimized synthesis of stable biogenic silver nanoparticles with uniform size distribution and average size about 20–30 nm. The synthesized Ag NPs exhibit the excellent catalytic activity by the complete reduction of 4-NP into 4-aminophenol with ultrahigh speed. Thus, this study explores a simple, greener and cost effectively approach for the synthesis of biogenic silver NPs and applicability of these NPs for the removal of toxic pollutants from the water resources.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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