

# Eco-friendly approach for synthesis of AgNPs and their catalytic application toward 4-nitrophenol to 4-aminophenol reduction

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The present work emphasises on the synthesis of silver nanoparticles (AgNPs) through the treatment of aqueous solutions of Ag nitrate with commonly available sugars, i.e. sucrose as reducing agents. The average particle size, morphology and elemental composition of the NPs are studied through transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy and ultraviolet–visible (UV–vis) spectroscopic techniques. UV–vis absorption spectroscopy confirms the formation of AgNPs with the strong absorption band at 408 nm. TEM reveals the spherical nature of synthesised AgNPs with a size range of 25–40 nm. Furthermore, catalytic potential of the NPs was examined for reduction of 4-nitrophenol (4-NP) to 4-aminophenol in the alkaline medium by using UV–vis spectroscopy. Complete reduction of the 4-NP was achieved within 35 min, thus validating the efficacy of AgNPs as an efficient catalyst. These catalytic capabilities firmly advocate the applications of AgNPs in the purification of polluted water.

**1. Introduction:** There are many compounds that do not cooperate during their reduction processes; however, among these compounds, the reduction of nitro derivatives endures immense confrontation, due to toxin features of these compounds [1–3]. Here, 4-nitrophenol (4-NP) is a phenolic compound having structure consisting of two nitro groups that are placed diagonally of the hydroxyl group on the benzene ring. The reduction process of 4-NP and other nitroaromatics is notably momentous as they are hazardous and terminating in nature [4]. Here, 4-NP and its by-products are being employed for application synthesis of herbicide, insecticides and chemical dyes which ultimately possess a threat to environment owing to their carcinogenic behaviour [5, 6]. Thus, the reduction of 4-NP into harmless by-products is highly important. In the past two decades with the rapid and prosperous growth of nanotechnology, the borohydride reduction of 4-NP–4-aminophenol (AP) by metal NPs has established increasing attention because this reaction can be completed in aqueous solution under mild condition [7]. For instance, metal nanoparticles (NPs) are being employed in many fields such as an efficient catalyst due to their bizarre catalytic nature, in medicine and electronics [8–10]. Among these silver NPs (AgNPs) have been widely used in various applications such as catalysis [11], medicine [12] and as an antimicrobial agent [13, 14]. AgNPs demonstrate the great advantage of being used as an appropriate catalyst since they can show vivid catalysis in mild conditions and ambient temperatures [15]. Also, AgNPs employed as an effective catalyst for 4-NP–4-AP reduction, which is very crucial to alleviate the pollutants based on nitro compounds. There is a number of methods available for the synthesis of AgNPs such as chemical [16], electrochemical [17], laser ablation [18], synchrotron radiations [19] etc. However, conventional methods involve many noxious and expensive chemicals, which make them inefficient processes. Thus, the synthesis techniques require eco-friendly and cost-effective approaches to accomplish the today demand. Green synthesis approaches come up to fulfil these voids. Similarly, there are a number of studies which involves the green synthesis of AgNPs [20–26].

In this regard, we demonstrate the one step, eco-friendly and cost-effective process for the synthesis of AgNPs by sucrose and tested their catalytic potential for 4-NP–4-AP reduction. As in

this process, it does not embrace any toxic and expensive chemicals for the synthesis of AgNPs. Thus, this Letter gives new insights in the green chemistry field for the synthesis of metal NPs and their applications for purification of water.

## 2. Materials and methodology

**2.1. Materials:** All chemicals used in experimentation are of analytical grade and are used without any further purification. The material used for the synthesis of AgNPs included sucrose, sodium hydroxide (NaOH) and Ag nitrate ( $\text{AgNO}_3$ ). All these chemicals were procured from Sigma Aldrich. For the application part, sodium borohydride ( $\text{NaBH}_4$ ) and 4-NP were purchased from Merck, Germany. Distilled water was used all through the experiment.

**2.2. Synthesis of AgNPs:** First,  $10^{-2}$  M of  $\text{AgNO}_3$  solution was mixed with 0.3 g sucrose solution, then  $10\ \mu\text{l}$  of  $10^{-1}$  M of NaOH solution added. Afterwards, the resulted solution was continuously stirred and heated at  $55\text{--}60^\circ\text{C}$  for 30 min. At this state, the colour of the solution was changed from colourless to yellowish, which confirms the formation of AgNPs [27]. A stepwise synthesis procedure is illustrated in Fig. 1.

**2.3. Catalytic activity:** The catalytic reduction process of 4-NP was monitored by ultraviolet–visible (UV–vis) absorption spectra. Primarily, 0.5 ml of 0.2 M freshly prepared  $\text{NaBH}_4$  solution was

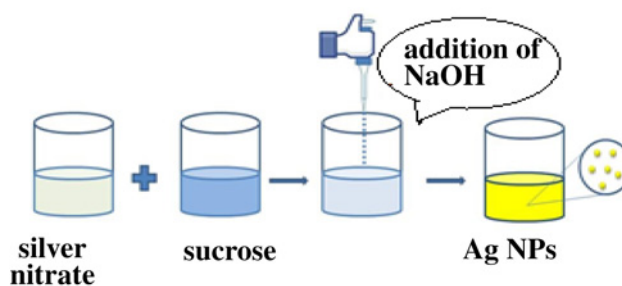
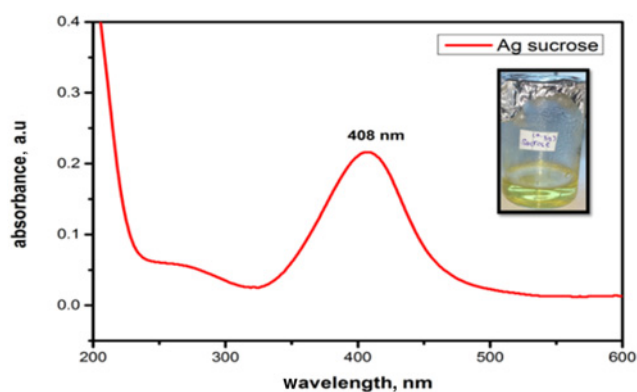
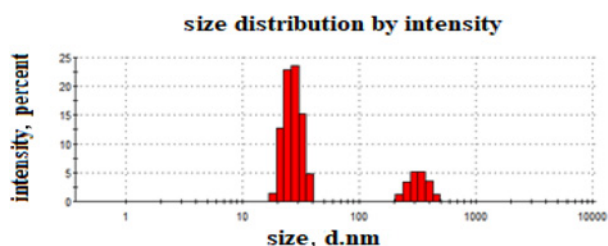


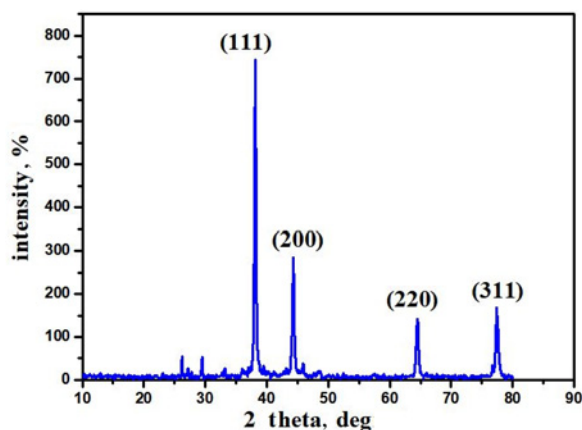
Fig. 1 Schematic representation shows the stepwise procedure for the synthesis of sucrose-mediated AgNPs



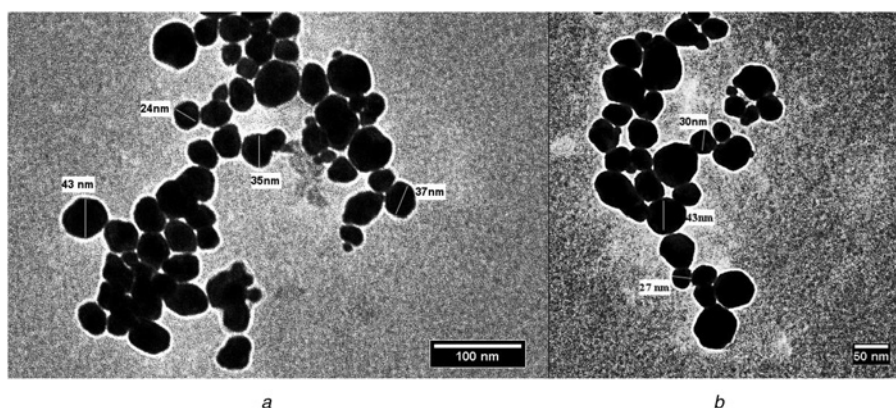
**Fig. 2** UV-vis spectrum of AgNPs (inset: photograph of synthesised AgNP's)



**Fig. 3** Histogram presentation showing the particle size distribution of AgNPs prepared by sucrose



**Fig. 4** XRD pattern of synthesised AgNPs



**Fig. 5** TEM images of sucrose-mediated AgNP's at  
a 100 nm scale bar  
b 50 nm scale bar

added to a solution containing 200  $\mu\text{l}$  of  $10^{-2}$  M 4-NP and 1.5 ml of deionised water. At this state, the 4-NP was converted into 4-nitrophenolate anion. After that, the different amount of catalyst was added and the reaction was spectrophotometrically monitored at different time intervals. A gradual change of the solution colour from bright yellow to colourless was observed during the reaction, which confirms the formation of 4-AP.

**2.4. Instruments:** Transmission electron microscopy (TEM) images of synthesised AgNPs were obtained by using Hitachi HF 3300. UV-vis spectrum of AgNPs was examined by using Shimadzu UV 2600 spectrophotometer. The intensity of the UV lamp used was set to 27  $\text{W/m}^2$ . The chemical composition of the synthesised sample was examined by using Oxford instruments energy-dispersive X-ray spectroscopy (EDX). For TEM analysis, grids were prepared by drop casting of 15  $\mu\text{l}$  AgNPs suspension on the carbon-coated copper grid and allowing them to dry in air. Particle size profile and polydispersity index (PDI) was determined by Zetasizer Nano (Malvern-ZEN-1690). The PANalytical X-ray diffractometer was used to obtain the X-ray diffraction (PXRD) pattern of the powder sample.

### 3. Result and discussion

**3.1. UV-visible analysis:** The reduction of Ag ions to AgNPs was confirmed by UV-vis spectroscopy analysis as shown in Fig. 2. When the sucrose and NaOH was added into the  $\text{AgNO}_3$  solution, the pale yellow colour was obtained. This colour occurs due to the observable effect of surface plasmon excitations in metal NPs [8]. The absorption spectra of AgNPs observed the sharp band around 408 nm in UV-vis spectra.

**3.2. Zetasizer analysis:** Dynamic light scattering which is based on the laser diffraction method with multiple scattering techniques was employed to study the average particle size of AgNPs. The prepared sample was dispersed in deionised water followed by ultra-sonication. Then, the solution was filtered and centrifuged for 20 min. Afterwards, the supernatant was diluted for four to five times and then the particle distribution in the liquid was studied in a computer controlled particle size analyser (Zetasizer Nano series, Malvern instrument Nano Zs). This Letter revealed that the Z-average size of biogenic AgNPs is 80 nm with PDI.0262 as shown in Fig. 3.

**3.3. PXRD analysis:** The phase and nanocrystalline size of synthesised AgNPs were determined by PXRD study as shown in Fig. 4. As XRD pattern shows the broad peaks corresponding to (111), (200), (220) and (311) planes with their respective  $2\theta$  angles at  $38.12^\circ$ ,  $44.30^\circ$ ,  $64.45^\circ$  and  $77.41^\circ$

(JCPDS Card No.: 89-3722). Thus, XRD study confirms the face-centred cubic structure of synthesised AgNPs.

The crystalline size ( $D$ ) of AgNPs was calculated using Debye–Scherrer's equation [24]

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where  $k$  is constant with value 0.9,  $\lambda$  is the wavelength of the incident X-ray beam,  $\beta$  is the full width at half maxima and  $\theta$  is the

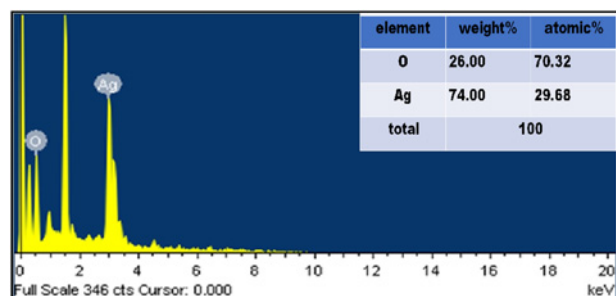


Fig. 6 EDX spectra of synthesised AgNP's

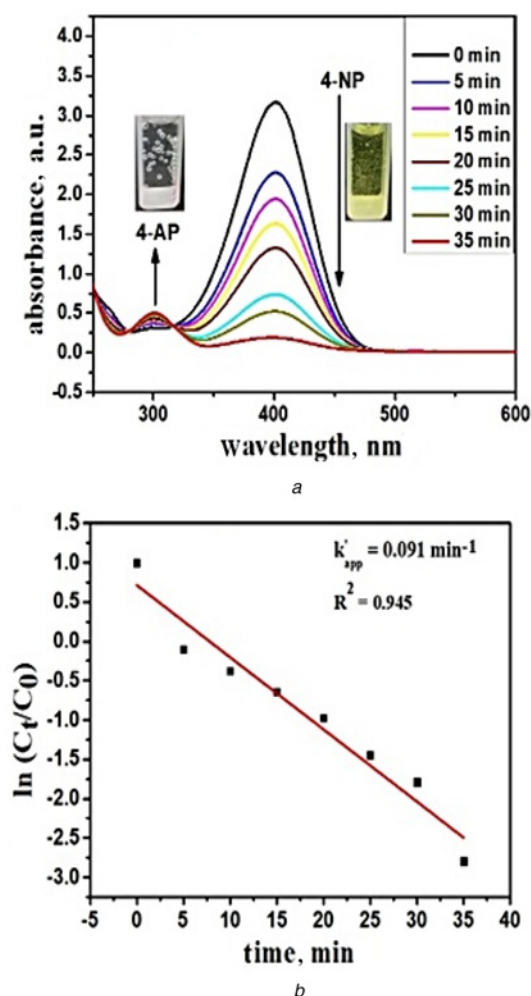


Fig. 7 Schematics illustrates the  
a UV–vis spectra illustrating AgNPs mediated catalytic reduction of 4-NP–4-AP in a time bound study  
b Linear relationship between normalised concentration ( $\ln C_t/C_0$ ) and reaction time

Bragg angle. The average crystalline size of AgNPs as determined from the above-mentioned equation was calculated to be 31 nm.

3.4. TEM and EDX analyses: For the structural and elemental analyses, the synthesised AgNPs were characterised by TEM and EDX. Figs. 5a and b show the spherical AgNPs with a size range of about 25–40 nm. Also, from Fig. 6, EDX analysis for chemically synthesised AgNPs shows 74% of Ag with 26% oxygen. Small traces of oxygen might be due to surrounding and the presence of biological moieties such as proteins and enzymes in plant extract [28].

3.5. Catalytic reduction studies: The catalytic activity of the as-prepared AgNPs was confirmed through reduction of 4-NP in the presence of  $\text{NaBH}_4$  as a reductant. After the addition of AgNPs as a catalyst, the reduction of 4-NP started immediately, and the colour of the reaction solution became lighter. The kinetics of the reaction was spectrophotometrically studied and presented in Fig. 7a. At  $t=0$  min, the UV–vis spectra of 4-NP was characterised by the presence of a sharp band at 400 nm owing to the formation of nitrophenolate ion in the presence of NaOH. Addition of AgNPs to the reaction medium accounted for the rapid decline in the absorption intensity at 400 nm simultaneously accompanied by the appearance of a relatively wider band at 298 nm indicating the formation of 4-AP [23]. However, without AgNPs, the reaction will not proceed further and there is no formation 4-AP in the presence of  $\text{NaBH}_4$  only [29]. This is due to abate in the activation energy barrier of the reaction. Since, small-sized AgNPs are responsible to decrease in activation energy barrier of the reaction; therefore, reaction will complete in short time period [30]. Within 35 min of the reaction duration, 4-NP was completely reduced to 4-AP which indicates 100% conversion of 4-NP as depicted in Fig. 7a.

3.5.1. Kinetic study: The dye degradation kinetics was investigated by using the pseudo-first-order rate law  $[\ln(C/C_0) = -kt]$ , where  $k$  and  $C_0$  are the rate constant and initial concentration at time  $t=0$ , respectively, and  $C$  is the concentration at any time  $t$ . A linear plot of  $\ln(C/C_0)$  versus time follows the pseudo-first-order kinetic model [31] (Fig. 7b) with an apparent rate constant ( $k'_{\text{app}}$ ) and  $R^2$  values of  $0.091 \text{ min}^{-1}$  and 0.945, respectively.

**4. Conclusion:** This Letter explores a cost-effective, one step procedure for the synthesis of AgNPs using sucrose as reducing and capping agents. Spectroscopic and microscopic studies affirmed the optimised synthesis of stable NPs with uniform size distribution and average size about 35 nm. The synthesised AgNPs show the excellent catalytic activity toward 4-NP–4-AP catalytic reduction. Also, the kinetics of the reaction of 4-NP follows the pseudo-first order with an apparent rate constant ( $k'_{\text{app}}$ ) and  $R^2$  values of  $0.091 \text{ min}^{-1}$  and 0.945, respectively. The current Letter thus explores a simple and cost-effective approach for synthesis and applicability of biogenic AgNPs for removal of toxin materials from water.

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