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Rapid and green microwave-assisted synthesis of silver nanoparticles using aqueous *Phoenix Dactylifera L. (date palm)* leaf extract and their catalytic activity for 4-Nitrophenol reduction

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Abstract
We have developed a fast and eco-friendly green microwave-assisted synthesis of silver nanoparticles (AgNPs) from silver nitrate solution using aqueous *Phoenix Dactylifera L.* leaf extract. Influence of reaction conditions such as extract solution concentration, Ag^+ concentration, pH and duration of microwaves treatment were investigated. Phytosynthesized silver nanoparticles of dimensions 20–60 nm were characterized using UV–visible spectroscopy (UV–vis), transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD). Efficient catalytic reduction of 4-Nitrophenol (4-NP) to 4-Aminophenol (4-AP) in the presence of $NaBH_4$ and colloidal silver nanoparticles was found.

Keywords: Green synthesis, Silver nanoparticles, Phoenix Dactylifera L., Catalytic Reduction, 4-Nitrophenol.

Introduction

In the last decade, nanostructured materials, particularly metal nanoparticles, have attracted much attention because of their unique properties, which are not observed when they are as bulk or molecules [1]. Among the metal nanoparticles, silver have attracted scientist attention due to its peculiar properties. A number of approaches are available for the synthesis of silver nanoparticles. For example, silver ions are reduced by chemical [2], electrochemical [3], radiation [4], photochemical methods [5], Langmuir–Blodgett [6-7] and green techniques [8]. Amongst these, green syntheses are not only a good way to fabricate benign nanostructure materials, but also to reduce the use or generation of hazardous substances to human health and the environment. This approach provides a facile and convenient entry to producing multiple inorganic nanoparticles. Many reports have been published in the literature on the green synthesis of silver nanoparticles using several plants extracts such as *Allium cepa* [9], *Artemisia annua, Sida acuta* [10], *Malus domestica* [11] and *Punica granatum* juice [12].

Bandyopadhyay et al. [13] reported the green synthesis of silver nanoparticles using *Phoenix dactylifera L.* seed and *Eisa et al.* [14] reported the green synthesis of gold nanoparticles using *Phoenix dactylifera L*. leaf. Herein, we report a rapid, green and eco-friendly method under microwaves irradiation conditions for the synthesis of silver nanoparticles using leaf extract of *Phoenix dactylifera L. (date palm)*. We also investigated the effects of green synthesis conditions such as the extract quantity and duration of microwaves treatment on the rate of AgNPs synthesis. The process is described by different analytical techniques including UV–visible spectroscopy (UV–Vis), transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD). Catalytic activities of the synthesized AgNPs have also showed for the sodium borohydride reduction of 4-Nitrophenol at room temperature.

2. Materials and methods

2.1. Materials & Instruments

Silver nitrate ($AgNO_3$, ≥99.0%), sodium borohydride ($NaBH_4$) and 4-Nitrophenol of analytical grade were purchased from Sigma-Aldrich. *Phoenix Dactylifera L.* leafs used in these experiments were collected from date palms of Errachidia region, South of Morocco.

Microwaves (Mars-5, CEM) were used as a heating source in order to take advantage of rapid synthesis of AgNPs under microwaves irradiation. The absorption spectra were collected using a UV-Vis scanning spectrophotometer model (VWR® UV-3100PC). The samples were measured against distilled water as reference and all experiences are worked under dark conditions.

2.2. Preparation of leaf extract of Phoenix Dactylifera L.

Phoenix Dactylifera L. leaves dried were powdered, sieved and stored in the form of fine powder (d<60 μm). 0.3 g of Palm leaf powder obtained were extracted with 25 mL of distilled water under Microwaves treatment (300 W). After cooling at room temperature, reddish brown extract was filtered using Whatman filter 0.45 μm and stored at 5 °C for future experiments.

2.3. Synthesis of Silver Nanoparticles

In a typical reaction procedure, the silver nanoparticles was synthesized by the addition of 1 mL of *P. Dactylifera L.* leaf extract to 10 mL of silver nitrate solution (0.005 - 0.1 mol/L). The mixture was placed under microwave radiation at 300 W for 30 s, 1 min, 2 min and 3 min of time.

2.4. Procedure for the catalytic reduction of 4-Nitrophenol to 4-Aminophenol

An aliquot of 4-Nitrophenol solution (1 mmol/L, 0.1 mL) was treated with freshly prepared Sodium Borohydride solution (16.5 mmol/L, 1.85 mL) and treated with 150 μL of *P. dactylifera L.* leaf extract derived colloidal silver nanoparticle. After the addition of of silver coloid, reduction is ascertained by recording the UV-visible spectra.

3. Results and discussions

3.1. UV-Visible spectroscopy Studies

The colorless $AgNO_3$ solution turned brown to deep red indicate the formation of AgNPs. The appearance of the brown color was due to the excitation of the surface plasmon vibrations, typical of AgNPs having maximum wavelength values, which were reported earlier in the visible range of 400–500 nm [15]. Figure 1 exhibits the appearance of characteristic peaks AgNPs at 420 nm for the four studies witch confirm the formation of AgNPs. To investigate the influence of extract concentration, we prepared four solutions from the first aqueous solution *Phoenix Dactylifera L.* leaf extract prepared using dilution 1/4, 3/4, 5/4, 8/4 noted C1, C2, C3 and C4 successively. 10 mL of a solution of $AgNO_3$ (0.1 mol/L) solution was added to each solution of the extract. Figure 1(a) shows that quantity of reduced silver is regularly increases with the concentration of extract solution, thus reducing Ag^+ ions to $Ag^{(0)}$ is provided by the molecules of the extract. Figure 1(b) shows the UV–vis spectra of the AgNPs obtained on varying the Ag^+ concentration (0.005, 0.01, 0.05 and 0.1 mol/L) and 1 mL of the *P. Dactylifera L.* leaf extract. As the concentration of Ag^+ increased, the surface Plasmon peak for AgNPs became distinct with an increasing concentration of Ag^+. The Plasmon bands are broad with an absorption tail in the longer wavelengths as concentration of Ag^+ increases, which indicated enhancement in size of the particles. To observe the effect of pH of the reaction mixture witch was varied as 3, 5, 7, and 9. As shows Figure 1(c)**,** the optimum pH value for synthesis of AgNPs is located on the basic area, and a maximum yield is showed at pH=9 with sharp peak at about 420 nm. It’s seen from Figure 1(d) that the yield of the synthesis of AgNPs increases with increasing duration of the radiation.

3.2. TEM and XRD studies

A transmission electron microscopy (TEM) was employed to assess the size, size distribution and shape of the formed silver nanoparticles. The transmission electron microscope micrograph displayed that the AgNPs were mostly spherical ranged from 20 to 60 nm, and average size estimated was 40.13 nm according to the size distribution shown in Figure 2.

The XRD patern of Silver nanoparticles obtained in the present study after reaction is shown in Figure 3. The diffraction peaks at 2θ = 38,20 °, 44.40 °, 64.59 ° and 77.50 ° assigned to the (111), (200), (220) and (311) planes of a faced center cubic (FCC) lattice of silver respectively and suggest that the AgNPs which were in good agreement with reference to the unit cell of the FCC structure (JCPDS File N^o 00-001-1167).

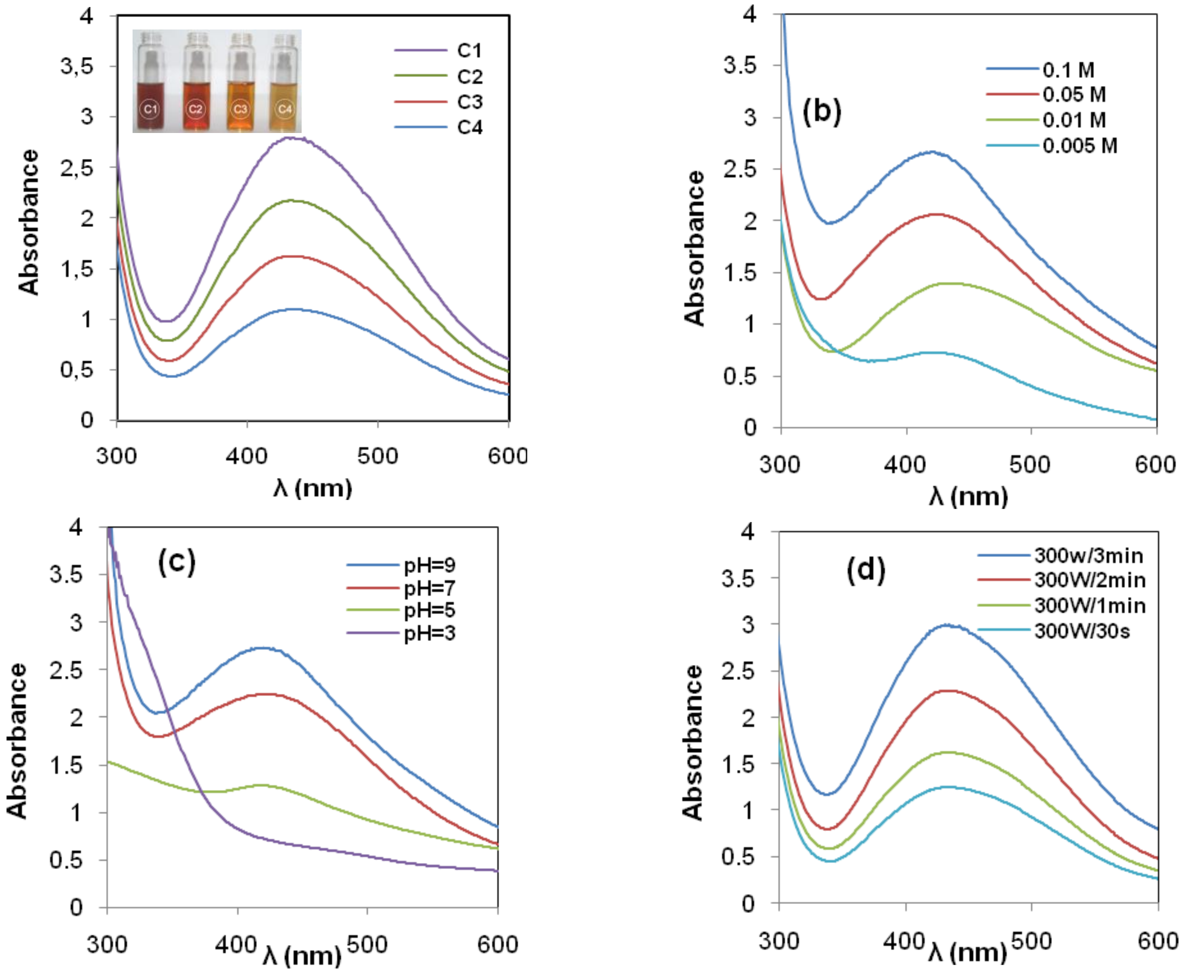

Figure 1: UV–visible absorption spectra showing the effect of concentration of P. Dactylifera L. leaf extract (a), concentrations of aqueous solution of $AgNO_3$ (b), pH (c) and duration effect of microwaves radiation (d) on absorption.

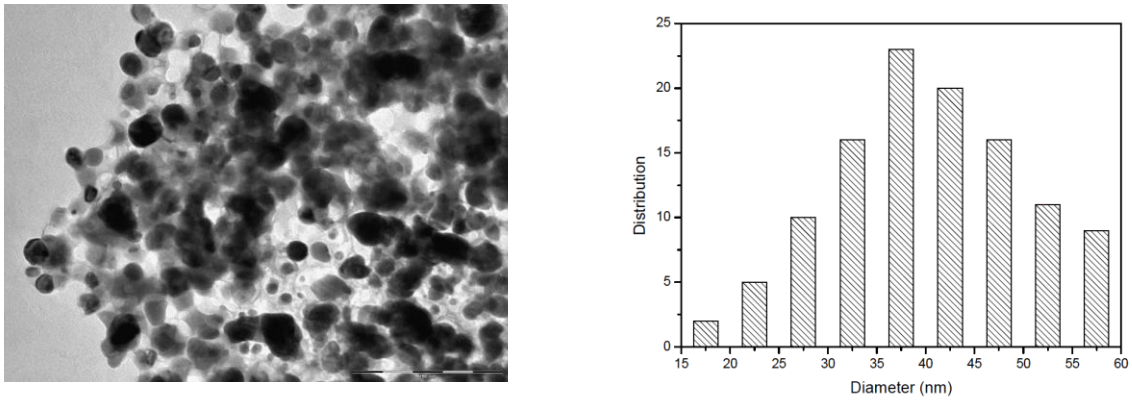

Figure 2 : Transmission electron micrograph and particle size distribution histogram of stabilised silver nanoparticles.

The average particle size was estimated using the well-known Scherrer formula, D = k λ / b cos (θ), where D is particle diameter, k is a constant equals 1, λ is wavelength of X-ray source (0.1541 nm), b is the full width at half maximum (FWHM) and θ is the half diffraction angle. The particles sizes obtained from XRD line broadening was found to be around 39.57 nm, which well correlates with that, obtained from TEM. The unassigned peaks at 2θ = 27.90 °, 32.30 ° and 46.2 ° in the diagram are thought to be related to crystalline and amorphous organic phases. X-ray diffraction results clearly show that biomolecules present in *P. Dactylifera L.* extract can be used to reduce silver ions to silver nanoparticles in a rapid green synthesis process.

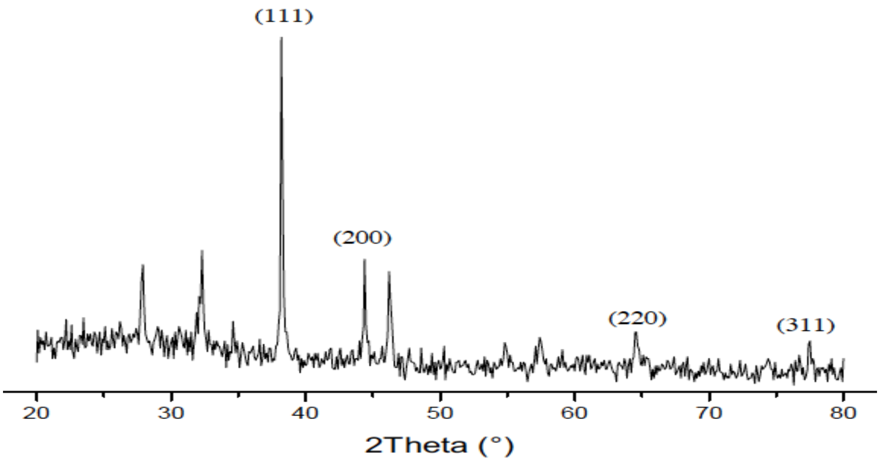

Figure 3 : XRD pattern of AgNPs phytosynthesized by treating $AgNO_3$ with *Phoenix Dactylifera L. leaf* extr*act*

3.3. Catalytic reduction of 4-Nitrophenol

Recently, several research groups have investigated the catalytic reduction of 4-Nitrophenol with $NaBH_4$, using a number of noble metal nanoparticles [16–26]. In order to study the catalytic activity of the as synthesized particles, 4-Nitrophenol aqueous solution was mixed with freshly prepared aqueous solution of $NaBH_4$ in a standard quartz cuvette. To this reaction mixture, 0.3 mL of AgNPs solution was added.

The progress of the reaction was monitored spectrophotometriclly by recording the absorption spectra at various time intervals. Treatment of an aqueous solution of 4-NP with freshly prepared aqueous solution of $NaBH_4$ shifted the absorption peak at about 318 to 400 nm due to the formation of 4-notrophenolate ions **(**Figure 4(a)**).** Without adding a catalyst, the color of the solution remained yellow-green. While, after the as prepared AgNPs were added, the peaks at 400 nm gradually disappeared. In contrast and as show Figure 4(b), new peak at 300 nm gradually under development, corresponding to the adsorption of 4-Aminophenol [27-28]. The color of the solution turned from green-yellow into colorless. In the intermediate stage of reduction the peak due to the $Ag^{(0)}$ Plasmon band could not be observed which remained masked within the absorption band of the nitro compounds but finally a new peak appeared at about 370 nm due to $Ag^{(0)}$ Plasmon band appeared [17]. Since the reaction was conducted under a large excess of $NaBH_4$, the reaction rate was nearly independent of the $NaBH_4$ concentration, and consequently the kinetics can be modeled by a quasi-first-order process with regard to the concentration of 4-Nitrophenol. Using the UV-visible data at different time intervals, the catalytic rate constant (k) for the reduction reaction was calculated to be 2.36 10^{-3} s^{-1}.

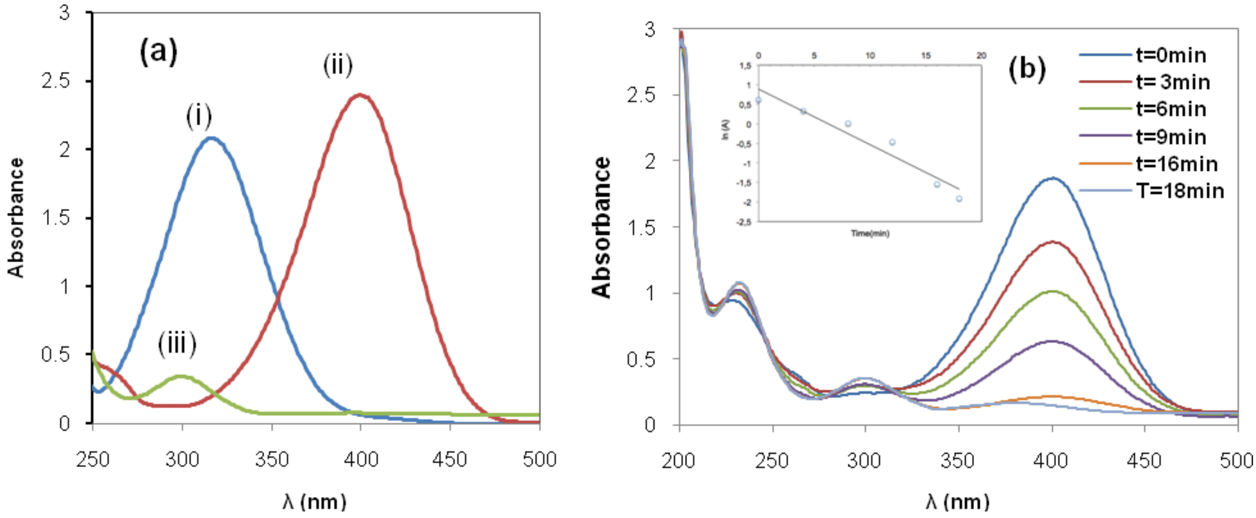

Figure 4 : (a) UV-Visible spectrum of (i) 4-Nitrophenol, (ii) mixture of 4-Nitrophenol and $NaBH_4$, and (iii) 4-Aminophenol. (b) Overlay of UV-Visible spectra as a function of time and ln(A) versus time during catalytic reduction of 4-Nitrophenol to 4-Aminophenol.

Conclusion

In summary, a rapid and green eco-freindly microwave-assisted synthesis of silver nanoparticles using aqueous solution of *Phoenix Dactylifera L.* leaf extract has been developed, which provide simple and efficient ways for the synthesis of nanoparticle. AgNPs prepared in this process are quite fast and low cost. The characterization of Ag^+ ions exposed to these plant extracts by UV-vis and XRD techniques confirm the reduction of silver ions to silver nanoparticles by biomolecules present in the *P. Dactylifera L.* leaf extract. The TEM image suggests that the particles are mostly spherical shaped. The synthesized silver nanoparticles have been utilized as an efficient catalyst for sodium bohydride reduction of 4-Nitrophenol to 4-Aminophenol at rom temperature.

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