GREEN SYNTHESIS OF COPPER OXIDE NANOPARTICLES BY PHEONIX DACTYLIFERA *L* LEAVES EXTRACT

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Green synthesis of metal nanoparticles (NPs) has attracted considerable attention because of its cheaper protocols and more environmentally friendly than standard synthetic methods. In the present paper, *Phoenix dactylifera* L extract was used to synthesize copper oxide nanoparticles with a differentvolume ratiobetween plant extract and metal (1mL of the plant extract to 100mL of 1mM $CuSO_4.5H_2O$).The obtained copper oxide nanoparticles were characterized by UV-Vis, FT-IR, XRD, SEM, and EDAX techniques. UV-Vis spectra showed a maximum absorption at 275nm related to the copper oxide.FT-IR spectra exhibit a weak peak at 554 cm^{-1} attributed to CuO vibration, confirming the formation of CuO nanoparticles. In addition, a disappearance peaks at 3264$cm^{-1}$from the solution of as prepared (NPs) reveals that polyphenols are responsible for thecopper oxide NPs formation. XRD confirmed the crystalline natureof CuO and Cu_2O NPs with average size ranged in 22-28 nm. SEM survey shows that the obtained nanoparticles having in general aspherical shape. As established by EDAX to confirm the presence of copper and oxygen, the weight percentage of the latterwas (72.39% Cu and 27.61% O), respectively.

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1. Introduction

During the later decade, sciences and technology development are characterized by many studies on the properties of nanosized objects and their elaboration by different methods for their practical application [1].

Nanotechnology is one of the most active fields of research in materials science [2], and may be defined as an intersection of technologies including different domains [3]. It is a great favor for humanity because its importance has covered the way for numerous applications in therapeutics [4], catalysis [5], microelectronics and biological sensors [6].

Recently, the nanoparticles have received significant attention because of their applications in many fields [7] and their atomic or molecular particles with at least one dimension between 1 and 100 nanometers which show new properties compared to bulk materials [8,9,10,11]. Based on their size, shape, morphology, and the large surface to volume ratio [12], nanoparticles possess has differences in both of their chemical and physical methods [13].

The common application of metallic nanoparticles is attributed to the great number of their unique properties in the various processes available for the synthesis of nanoparticles [14]. Physical and chemical methods are currently used to synthesize nanoparticles with desired properties [15, 16]. However, these production methods are usually expensive, labor-intensive, and

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can be hazardous to the environment and organisms [14]. So looking for other friendly techniques such as green synthesize has received great attention from researchers to develop green chemistry and bioprocesses [17]. Many resources existing naturally for the synthesis of metallic nanoparticles are bacteria, fungi, algae, virus, yeast and plants [18]. The latter is considered as a best candidate for the synthesis of these nanoparticles from other biological processes due to their free toxic chemicals, as well as their providing natural capping agents [19, 20].

Recently, among the metal oxide nanoparticles, copper oxide nanoparticles have attained significant importance because of their distinctive properties [21], and their varied range of applications such as, solar cells [22], gas sensors [23], catalytic [24], optical [25], hydrogen storage materials [26], and medical applications [27].

In this study, green synthesized copper oxide nanoparticles using a *Phoenix Dactylifera L* leaf extract (see Fig. 1), was investigated. Characterizations of the obtained nanoparticles were analyzed by standard techniques such as UV-Vis,FT-IR, XRD, SEMand EDAX.

Fig.1. Leaves of Phoenix dactylifera L.

2.Materials and methods

2.1 Plant material and extraction

Leaves of *Phoenix dactylifera* L were collected from local fields in the region of El Oued (South east of Algeria). Fresh leaves were washed and dried in a shade under room temperature for 15 days. The extraction of plant materials was carried out following the maceration method. 10 gram of the powdered material was then extracted using 70% ethanol in Erlenmeyer flasks (150 ml), and the ratio of plant material mass to solvent volume was 1:6. Before its use, the mixtures were kept for 24 hours in tightly sealed vessels at room temperature.

2.2 Synthesis of copper oxide nanoparticles

Copper oxide nanoparticles were synthesized through a reduction of copper sulfate by the phenolic compounds of leaf extract. The reaction mixture was prepared by adding 1mL of the plant extract to 100mL of 1mM $CuSO_4.5H_2O$ solution in a 250 mL flask. The reaction was carried out using reflux mounting under continuous stirring at.70°C for 2 hours. The formation of copper oxide was confirmed by a color change from green to dark brown.

The brown solid product was collected by centrifugation at room temperature and washed several times with absolute ethanol and distilled water. The product was dried over night at 80 °C then is heated in a furnace at 400°C for 2 hours. The annealed powder considered the samples of our study. Effects of plant extracts were studied and several experiments were carried out by changing the volume ratio between plant extract and copper sulfate1:100, 1:90, 1:70, 1:50, and 1:30 respectively, under the same experimental conditions.

2.3 Characterization of copper oxide nanoparticles

The following techniques were employed for the characterization of copper oxide nanoparticles: UV-Vis, FT-IR, XRD, SEM, and EDAX.

UV-visible absorption spectroscopy plays a very important role to investigate the optical properties of nanoparticles [28]. The optical property of copper oxide nanoparticles was analyzed by the cited technique, which is Shimadzu apparatus (Shimadzu-1800 working in the wavelength

range 200-900nm). The analysis was performed in a quartz cell, using distilled water as a reference solvent.

The functional groups of the extract and chemical composition of the nanoparticles were determined by FTIR spectrophotometer (Nicolet iS5, Thermo Fisher Scientific) in the spectral range 400-4000cm^{-1}.

The structure and grain size of copper oxides were examined by XRD techniques using X-ray diffractometer (Rigaku Miniflex 600) with a Cu-Kα (λ = 1.5406 Å) in the2θ angles ranging from10° to 80°.

The shape and morphology of the nanoparticles were examined using scanning electron microscopy (SEM-TESCAN VEGA 3) equipped with an energy dispersive X-ray analysis (EDAX).

2. Results and discussions

Copper oxide nanoparticles synthesis was carried out using novel, environmentally kind synthetic strategy by means of leaves from *Phoenix dactylifera* L as described in Fig. 1.

The preliminary phytochemicals screening of Phoenix dactylifera L leaves extract shows the existence of polyphenols, flavonoid and condensed tannin [29].

The UV-Vis spectra of copper oxide nanoparticles synthesized using a *Phoenixdactylifera* L leaf extract are shown in Fig.2. As can be seen from this figure, two peaks of maximum absorption are exhibited. One is strong at about 275nm with another weak peak at 349nm [30], which are attributed to the formation of copper oxide. An increase in the intensity of the peaks with the ratio decrease is observed. This may be due to the increasing number of nanoparticles formed as a result of copper ions reduction [31], which may be caused by the complete enlacement of the copper ions by the extract.

As mentioned in the experiment part, the change in color from green to dark brown. This change in color may be owing to the excitation of surface plasmon absorption of copper oxide [32], which was generated by a coupling between the conduction electrons oscillation modes and the incident electromagnetic radiation [28].

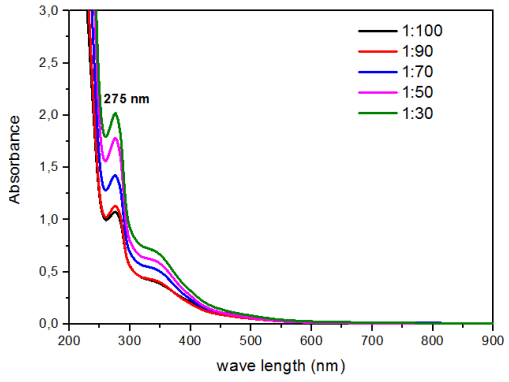

Fig. 2. UV–Vis absorption spectrum of copper oxide nanoparticles synthesized withvolume ratio 1:100, 1:90, 1:70, 1:50, and 1:30.

The FT-IR analysis was usedfor both the *Phoenix dactylifera* L leaf extract and the solution of as synthesized copper oxide nanoparticles to identify the possible biomolecules responsible for the bioreduction of the copper oxide nanoparticle.

Fig. 3 gathers the FT-IR spectrum of *Phoenix dactylifera* L leaf extract with different spectra of nanoparticles prepared with different ration. Fig. 3(a) shows the FT-IR spectrum of *Phoenix dactylifera* L leaf extract, this spectrum depicted some peaks at 3264, 1605, 1442, 1283 and 1049cm^{-1}. The broad band, at 3264 cm^{-1}, is due to the O−H group stretching vibration [33].

The absorption peaks situated around 1605 and 1442 cm^{-1}correspond to the stretching vibrations of C=C, C−C, and C−O of the aromatics cycles [34]. Weak bands at 1283 and 1049cm^{-1}indicate the presence of C−H and C−O stretching of alcohols, carboxylic acids, ester and, ether groups respectively [35]. Because of the presence of the mentioned functional groups inside the structure of polyphenols, the spectrum reveals the presence of phenolics in the plant extract [36].

By comparing the spectrum of the as synthesized copper oxide nanoparticles each other, Fig. 3 b-fshows a weak peaks at 512 and 618 cm^{-1}which are attributed to vibrations of CuO confirming the formation of copper oxide nanoparticles. Also a disappearance of the absorbance bands at 3264, 1605, 1442, 1283 and 1049 cm^{-1} of polyphenols from the solution after synthesing nanoparticles, leads us to proclaim that the leaves *Phoenix dactylifera* L extract has the main role in reducing the Cu ions and then stabilizing the copper oxide NPs.

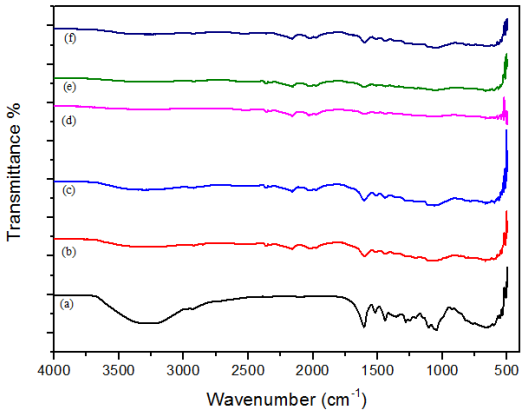

Fig. 3.FT-IR spectra of Phoenix dactylifera L leaf extract and as synthesized copper oxide nanoparticles solution with volume ratio a) leaf extract, b) 1:100, c) 1:90, d) 1:70, e) 1:50 and f) 1:30, respectively.

Fig. 4 represents the FT-IR spectrum of copper oxide nanoparticles synthesized from leaves of *Phoenix dactylifera* L. The absorption bands at 512 and 618cm^{-1} correspond to the stretching vibration of Cu-O bond in monoclinic CuO [37] as seen in the inset of fig. 4. The absorption peak appearing at 1596cm^{-1} may well be correlated with the bending and stretching vibrations of adsorbed water [38]. It is worth noting that the absorption band of Cu−O becomes greater than those obtained from the as synthesized solution of copper oxide nanoparticles revealing that the annealing treatment ameliorates the oxide copper nanoparticles.

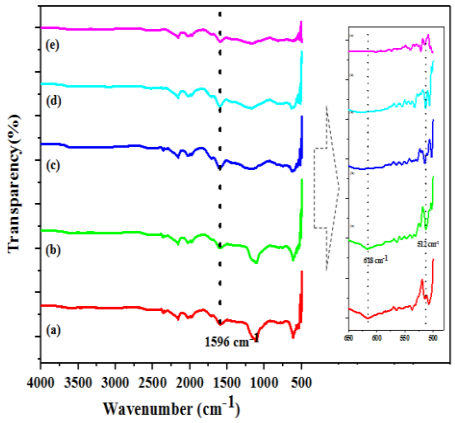

Fig. 4. FT-IR spectra of annealing at 400 °C synthesized copper oxide nanoparticles obtained from volume ratio a) 1:100, b) 1:90, c) 1:70, d) 1:50 and e) 1:30, respectively. Inset of this figure focuses on Cu-O bonds

The Fig.5 a-e exhibits typical XRD patterns of synthesized copper oxide nanoparticles.Forgiven ratio (1:100, 1:90 *i.e* Fig.5 a and b), the spectrum indicate the presence of monoclinic cupric oxide (CuO) and Cu_2O mixture. As depicted by the peaks at 2θ values of 35.31°, 38.55°, 48.56°, 58.12°, 61.38°, 65.87° and 67.89° which correspond to the crystal planes of (*002*), (*111*), *(-202*), (*202*), (*-113*), (*022*), and (*113*) of CuO monoclinic phase, respectively. Those planes accord well with the (JCPDS Card No. 01-089-2529). Whereas the peaks at 2θ value of 29.85°, 36.44°, 42.29°, and 61.41° correspond to the planes (*110*), (*111*), (*200*), and (*220*) of cubic crystal structures of Cu_2O much well with the (JCPDS Card No. 01-078-2076).

For the ratio 1:50 and 1:70 (*i.e* Fig.5 c and d), the Bragg's reflection peaks observed at 2θ value of 29.85°, 36.44°, 42.29°, 61.41° and 73.39° correspond to the planes (*110*), (*111*), (*200*), (*220*) and (*311*) of Cu_2O cubic crystal structures and much well with the Joint Committee Powder Diffraction System (JCPDS Card No. 01-078-2076) confirming the formation of Cu_2O nanoparticules product. Finally for the sample 1:30 all diffraction peaks can be indexed to the monoclinic phase of cuprous oxide crystal CuO according to (JCPDS Card No. 01-089-2529).

The average particle size was estimated using the Debye-Scherrer equation [39].

$$d=k\lambda/\beta cos\theta$$

where,***d***: the particle size (nm),***k***: is a constant equation to 0.94,$\boldsymbol{\lambda}$: the wavelength of X-ray radiation (1.5406 Å) and $\boldsymbol{\beta}$ is the full width at half maximum of the diffraction peak (FWHM). The average crystallite size was found to be in the range 20-28 nm.

In Table 1, it was reported the variation of the crystallite size of the two NPs of Cu_2O and CuO as a function of the volume ratio of extract/copper sulfate. The crystallite of Cu_2O increases from 25.84 to 28.34nm passing by 26.56nm, then decrease to reach 23.62nm in the volume ration range of 1:100, 1:90, 1:70, and 1:50 respectively. Whereas the size crystallite of CuO decreases from 25.84 to 20.70nm with decreasing of the ratio from 1:100 to 1:90, then increase to reach 28.8nm for the ratio 1:30.

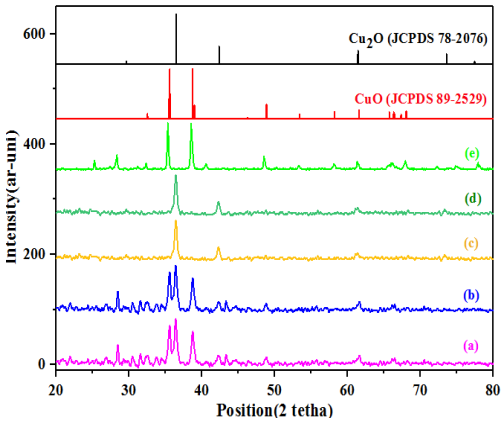

Fig. 5. XRD patterns of copper oxide nanoparticles synthesized at different volume ratio (a) 1:100 (b) 1:90 (c) 1:70 (d) 1:50 and (e) 1:30.

Table 1. Size of copper oxide nanoparticles synthesized at different volume ratio (a) 1:100 (b) 1:90 (c) 1:70 (d) 1:50 and (e) 1:30.

Samples	CuO nanoparticles size (nm)	Cu_2O nanoparticles size(nm)
a	25.84	25.00
b	20.70	26.56
c	///	28.34
d	///	23.62
e	28.38	///

Fig. 6(a-e) exhibits SEM images of the synthesized copper oxides nanoparticles. It is clearly shown that in general the particles are roughly spherical and irregular shaped, which are free from agglomeration. For the mixture of CuO and Cu_2O nanoparticles (Fig. 6 a and b), it is observed that almost of them are spherical in nature; further, the particles are agglomerated to form foam like bunch of particles. For Cu_2O nanoparticles (Fig.6 c), it is observed that there is more than one shape (spherical nanoparticles) as depicted in SEM image. The nanoparticles become greater in dimension having the form of foam like bunch (Fig. 6 d). But in Fig. 6 e, they are greater nanoparticles but turned into only spherical shape.

Further analysis of copper oxide nanoparticles, by EDAX, as shown in Fig. 5f confirms the presence of copper andoxygen, with the weight percentage of about 72.39% Cu and 27.61% O. This analysis showed also a doublet signal peak for copper at 1 and 8keV.

As result to this green synthesized NPs, it seems to us that the concentration of plant extract plays a key role in reducing and stabilizing the copper oxide NPs. It has found that by increasing the concentration of plant extract, the shape, size and nature of nanoparticles change too hence CuO and Cu_2O nanoparticles were obtained. Cu_2O NPs change in the shape from spherical nanoparticles to a small agglomeration as shown in SEM image (Fig.6 c and d). While for the CuO NPs it was observed that the shape remains spherical with a change in size only as shown in SEM image (Fig. 6a, b, and e). By increasing the concentration of plant extract, the concentration of phytochemicals increased and the reduction of copper salt also increased leads to a complet oxidation of copper (sample of Fig. 6e). The green reduction of the copper salts starts rapidly, and the formation of copper oxide nanoparticles is indicated by changes in the color from green to the dark brown of the mixture solution. Based on the disappearance of the absorbance bands at 3264, 1605, 1442, 1283 and 1049cm^{-1} of polyphenols it seems to us that the latter has the foremost role in reducing the Cu ions and then stabilizing the copper oxide NPs.

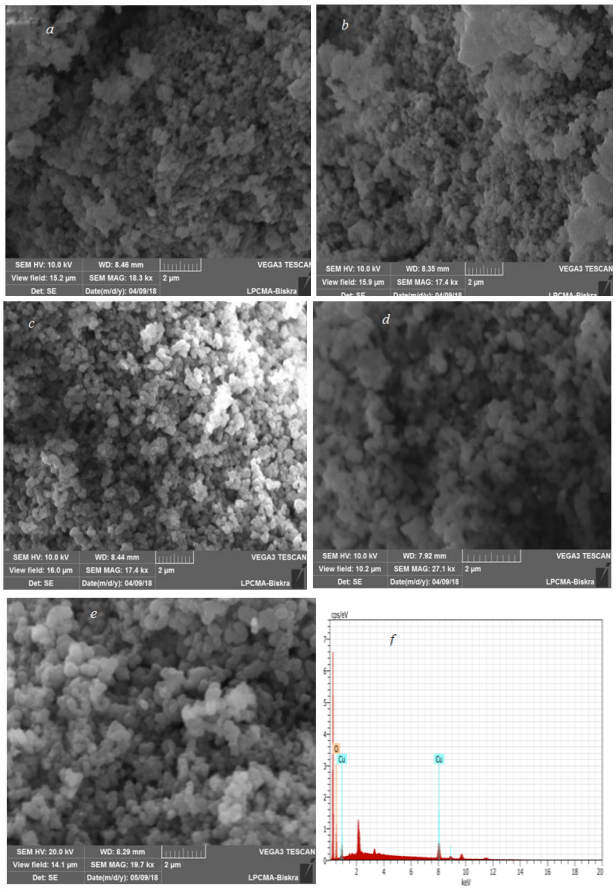

Fig. 6. SEM image and EDAX: (a-e) are SEM images and (f) is the EDAX of copper oxide nanoparticles.

3. Conclusions

In this work attemption to prepare copper oxide nanoparticles using *Phoenix dactylifera* L leaves from the region of El Oued (South east of Algeria) with different volume ration of extract to the copper sulfate was carried out. The formation of copper oxide was confirmed by different characterization techniques. Absorbance peak at 275nm was showed by UV-Vis indicating the formation of copper oxide, which it was confirmed by FT-IR study showing Cu-O absorption at 512 and 618cm^{-1}.

XRD studies displayed that a synthesized nanoparticle exhibits a cubic and monoclinic crystalline structure having an average grain size of 20-28 nm. SEM image showed that synthesized particles are roughly spherical shape. Also, this study indicates that copper oxide nanoparticle can be synthesized using a *Phoenix dactylifera* L leaf extract. This procedure is green and viable because of its ease, fast, low cost and friendly to the environment compared to other methods.

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