

Dates (*Phoenix Dactylifera* L.) extracts derived nanoparticles and its application

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ABSTRACT

Plant-mediated green synthesis of metallic nanoparticles (NPs) has become the most deserving alternative to chemical synthesis as this process is economical and energy-efficient, and environmentally benign. For the last twenty to thirty years, different plant sources are being utilized for the fabrication of green NPs, and few of them have used the extract of *Phoenix Dactylifera* L. as reducing, capping, or stabilizing agents. This review provides a detailed outline of the extraction method from various parts of dates and their synthesis with different metal salts using these extracts. The applied techniques of characterization and application of these nanoparticles have also been thoroughly discussed. The phytochemicals present in the extract were responsible for reducing the metals. Except for a few, all the investigations reported the spherical NPs but have variations in their size. These NPs have high prospects in applications such as antimicrobial, anticancer, antioxidant, and catalytic activities. This work may lead the path for additional advancement in this field, and researchers may take up the future work for the large scale production of NPs and their application using date extracts.

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1. Introduction

The term "nano" in science is labeled for one billionth part, i.e., 10^{-9} . The sizes of nanoparticles obtained from metals range from 1 to 100 nm.¹ The shapes, sizes, and compositions of metallic nanoparticles are considerably associated with their properties that have been exploited for their superior physical, chemical, mechanical, thermal, and biological properties as compared to the bulk materials.^{2,3} The main aim of the synthesis of nanoparticles (NPs) with control over particle size, shape, and crystalline nature is that it can be used for potential applications, such as bio-medical, biosensor, a catalyst for bacterial biotoxin elimination and lower cost electrode.^{4,6} Researchers have made an enormous effort in synthesizing metal NPs by applying different physical and chemical methods. However, all these methods utilize expensive as well as toxic reducing and stabilizing agents.⁷⁻¹³ They are also more likely to have toxic unreacted chemicals and by-products that make most of these synthesized NPs unfit for biomedical applications. Despite the advantages of metal nanoparticles synthesized from chemical means, there exist potentially worrying toxic effects.¹⁴ Industrial scale production and use of NPs may cause unintentional human and environmental exposure to these substances. Several researchers and social activists have raised their concerns about the environmental impact and toxicity of chemically synthesized nanoparticle-based products.¹⁵ Humans can get exposed to these chemically fabricated nanoparticles right from the origin of generation, transportation to final

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applications in different products.¹⁶ According to the Wilson Centre data, exposure to 45% of the 580 categorized NPs have been marked as potentially dangerous.¹⁷ The purposeful use of these chemically synthesized metallic NPs in many commercial products, such as vectors of drugs, sunscreens, toothpaste, cosmetics, plastic products, textiles, paints, and gasoline components, are likely source of human exposure and enters into the body through different routes, including injection, inhalation or ingestion. Consequently, an intoxicating number of organs and tissues, including the central nervous system.¹⁸⁻²¹ Ray and his coworkers²² have raised issues regarding the potential impact of emerging NPs that are chemically synthesized on the environment. Griffitt et al²³ reported the effects of particle composition on the toxicity of chemically produced metallic nanomaterials in aquatic organisms and observed that nanosilver and nano copper cause toxicity in all organisms tested 48-hr median lethal concentrations as low as 40 and 60 µg/L. The toxicity of gold nanorods is due to hexadecyl cetyltrimethylammonium bromide (CTAB), which is the most widely used surfactant for synthesizing nanorods.²⁴ The work by Karlsson et al²⁵ focussed on several chemically synthesized metal oxide nanoparticles (CuO, TiO₂, ZnO, Fe₃O₄, Fe₂O₃) and found that each of them has a varying degree of cytotoxicity and ability to cause DNA damage and oxidative stress. Many of the surfactants used to control and shape the nanoparticles' size are toxic, so there is a need to find alternatives to surfactants, templates, or other substances to stabilize and control nanoparticle shape during synthesis.²² There are encouraging results advocating the green nano synthesis can guide or design the production and application of greener nanomaterials across the range of compositions, sizes, shapes, and functionality. Therefore, the synthesis of nanoparticles seeks an eco-friendly approach and green materials for the current scenario.²⁶ Consequently, the need for environmental friendly molecules that provide solutions to growing challenges related to environmental issues led to a novel practice of using the green source for the synthesis of nanoparticles.²⁷ Green syntheses is generally carried out by using both eukaryotic and prokaryotic microorganisms such as yeasts, fungi, and bacteria or by utilizing templates like membranes, viruses DNA, and diatoms. The comparison of the different routes for NPs green synthesis is shown in **Table 1**.

Table 1. Different routes for NPs green synthesis

Plant route	Microorganism route	Green chemical route
Uses the plant part like leaf, stem, seed, shoot, root, petal, fruit, extract either fresh or dried; the extract of any of those plant parts in distilled water will carry the reducing and capping agent needed for fabricating the NPs.	Microorganism, either fungi or algae, or bacteria grows on culture media where it will release the reducing agent or the capping agent needed to reduce the metal ion	Eco-friendly pure chemicals like chitosan, starch, sucrose, calcium alginate are used as a capping agent to form spherical NPs.

But the most common method of green synthesis of NPs is through plants and their extracts. To synthesize nanoparticles at a larger scale, the plants have proved to be the ideal contender for reducing metal ions since the beginning of the 20th century. The phytochemicals present in the plant's extract can biologically reduce the metal ions and minimize the agglomeration and oxidation of NPs. Therefore, plants are considered as alternate reducing and capping agents in NPs synthesis. The use of plant extracts in the synthesis of NPs eliminates the complicated steps such as intracellular synthesis, multiple purification steps, maintenance of microbial cell culture, or prolonged incubation time, etc. Additionally, the plant-mediated synthesis is typically carried out at neutral pH and occurs at ambient temperatures.²⁸ It is also well established that NPs synthesized with plant source shows the best compatibility with biomolecules.²⁹ Green synthesis is one of the most popular methods due to the abundant availability of materials, simplicity, and safe to handle in addition to low cost and minimum toxic pollutants. The significant steps involved in this method are selecting eco-friendly reduction agents, H₂O as solvents are generally preferred, and non-toxic substances as stabilizers. According to the available literature, numerous parts of the plants such as leaves, fruits, barks, peels, roots, buds,

flowers, twigs, peel, latex, and seeds are extensively used in the synthesis of metal and metal oxide (silver, gold, platinum, titanium, iron, cobalt and nickel) nanoparticles of different sizes and shapes.³⁰⁻³⁶ Numerous research pieces have concluded that plant-mediated synthesis of metal NPs shows potential biological activity. Plant extract contains many bioactive and phytochemical compounds like flavonoids, iridoids, alkaloids, lignans, glycosides, phenolic acids, and etheric oils, benzenoids, quinoids, and steroids.³⁷⁻³⁹ Bioactive compounds present in plant extract are responsible for reducing metal ions and acting as capping agents for metal NPs exhibiting bacteriostatic effects.⁴⁰ Many biosynthesized NPs have been used to treat bacterial infections⁴¹ and are also useful in antitumor therapy.⁴² Plant extract–NP bioconjugates possess capable antioxidant activity and anti-inflammatory properties.⁴³ The possible array of sizes, shapes, and compositions of green synthesized NPs converts into a wide range of nanomaterial applications. We have seen considerable advancement in synthesizing NPs of the desired morphology and size during the last decades to make them application-specific. Innumerable green NPs have been synthesized using plant species varieties with Ag, Au, Pt, or Cu. They have their applications ranging from biomedical purposes to catalytic water treatment or as environmental sensors and many other applications. The NPs from the extracts of *Phoenix dactylifera* L. has also acquired adequate applications in antimicrobial, antioxidant, anticancer, and catalytic activities. However, much less research has been carried out for synthesizing metal NPs with the extracts of the different parts of the plant species date palm (*Phoenix dactylifera* L.), as evident from **Fig. 1**. Considering the scarcity of detailed work, this review has been motivated to disseminate up-to-date information on the methods of extraction from different parts of the date palm, synthesis of Ag, Au, Pt, Zn, Cu, Pd nanoparticles prepared using date palm extracts, the characterization techniques involved, and some prospects on the potential applications in future.

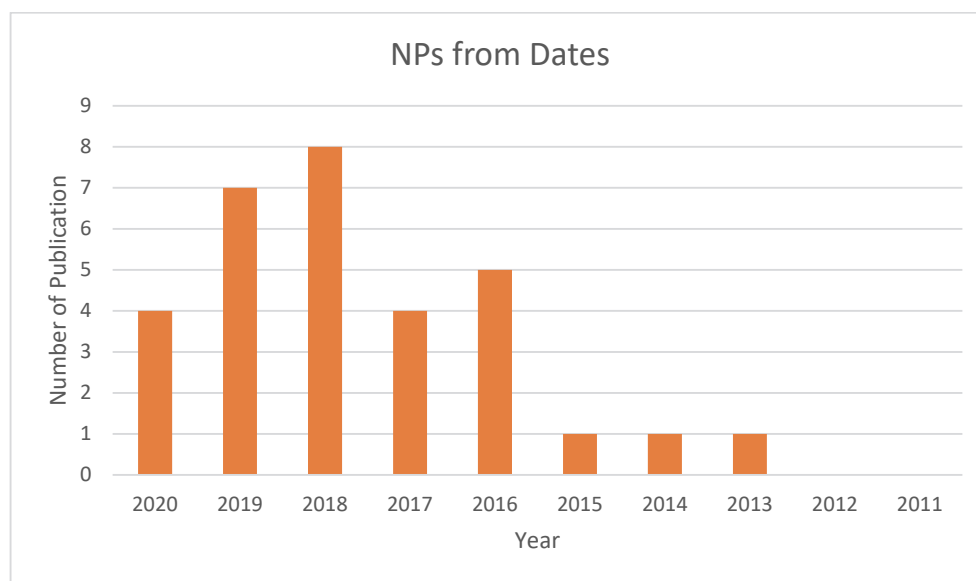


Fig. 1. Number of Publications for the synthesis of NPs from dates

2. Date Palm Tree

Date palm tree (*Phoenix dactylifera* L.) is considered one of the oldest and main staple ancient crops in the *Arabian Peninsula*. Date palm belongs to the *Arecaceae* family (Angiosperms, monocotyledon), consisting of about 200 genera and more than 2,500 species. The date palm fruit is an important staple food resource in the Middle East and Asia because of its sweet taste. It has had a considerable effect on people's daily lives of the *Arabian Peninsula* for a long. Due to the fast-growing demand, and economical production of the dates has increased over the years. Worldwide dates are cultivated on about 2.9 million acres of land in around 35 countries.⁴⁴ *Phoenix dactylifera* L. is one of the genera which are native to the tropical or subtropical regions. The name of the species *dactylifera* means "finger-bearing," which refers to the fruit clusters produced by this plant.⁴⁵ The uniqueness of

the date palm tree led them to adapt to adverse circumstances. Date palm trees are generally cultivated in the sand and grown in soil where soil water is near the surface. The quality of soil and water influences the date palm tree's growth as its optimum growth is found where soil water is close to the surface, whereas its growth is not found in saline conditions. *Phoenix dactylifera* L. has an average height of around 30 m and is considered the tallest of all the date palm species. The size of the fruit ranges to 100 mm × 40 mm.⁴⁶ The fruits of the date palm contain a single seed enclosed by a fleshy pericarp. They are usually oblong; however, some varieties may have nearly spherical shapes consisting of several nutrients like carbohydrates, proteins, fat, minerals, and vitamins.⁴⁷ Fruits of *Phoenix dactylifera* L. possesses phytochemicals as shown in **Fig. 2**, such as carotenoids, polyphenols, phenolic acids, isoflavones, lignans, flavonoids, tannins, and sterols⁴⁸ that may provide antioxidant, antimutagenic, free-radical scavenging, antimicrobial, and immunomodulatory medicinal properties.⁴⁹⁵⁰ The leaves of date palm trees are elongated and are divided into leaflets and rachis. Every year, the date palm tree gives rise to nearly 10-20 new leaves to adapt to hot and dry conditions.⁵¹ The cellulose content in date palm leaves is more than that of lignin, making it appropriate for automotive applications.⁵² The date palm leaves are also used as a traditional medicine for the treatment diarrhea, intestinal hemorrhage, jaundice, and diabetes.^{53, 54} Date palm seeds are one of the bulk residues produced by date palm trees annually. The seeds are also utilizable, but a few studies investigated their use in some applications. The date seeds constitute only 8-15 % of mass to that of the date palm fruit.⁵⁵ Substantial amounts of dietary components like oleic acid, polyphenols, and dietary fibers are present in date seed in addition to many minerals. Date seeds are commonly used in traditional medicine for the treatment of diabetes, hypertension, gastrointestinal, and cardiovascular disorders as well as to boost the immune system.⁵⁶

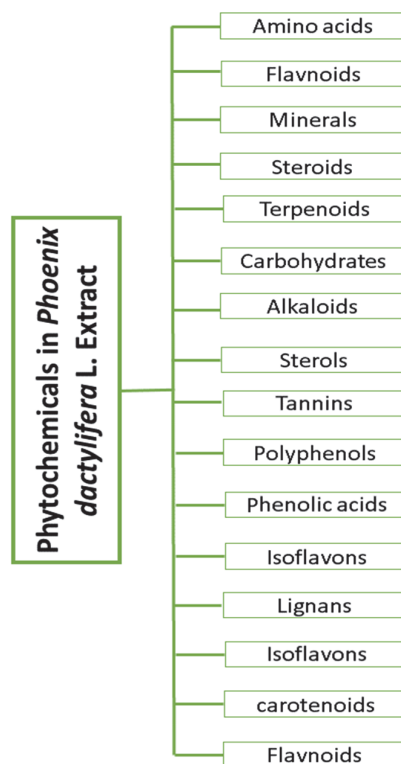


Fig. 2. Phytochemicals present in extracts from different parts of *Phoenix dactylifera* L.

3. Methods of Extraction from *Phoenix Dactylifera* L

The extract's preparation depends on which part of the date palm plant has been employed in the experiment because the concentration of the phytochemicals present in the extract may differ. The extraction methods may vary even if the different parts of the same date plant are being used. In this

part, we summarized the standard techniques applied for extraction from the fruits, seeds, leaves, or pollens of *Phoenix dactylifera* L. as discussed in the literature for synthesizing different metal NPs.

3.1 Preparation of fruit extract of *Phoenix Dactylifera* L

The preparation of *Phoenix dactylifera* L. fruit extract usually has been reported by two main methods. Some workers reported the first method for the extraction Zafar et al,⁵⁷ Al-Radadi,⁵⁸ Abusahid and Kandiah,⁵⁹ Zaheer,⁶⁰ in this method they have taken the fruits of *Phoenix dactylifera* L. which were repeatedly washed with running tap water and then with deionized water to remove dust and soil particles and to sterilize some even use Tween 20. The dates are dried to remove the traces of water at room temperature or in the oven at 50 °C, followed by weighing and then chopping into fine pieces. The chopped date fruits were soaked in about 250 mL distilled water, and the solution is stirred and heated at 60°C for around 30-40 min and filtered through Whatman filter paper No. 1 twice. The resultant extract used as reducing and stabilizing agents was stored in amber bottles and kept in the refrigerator at 4 °C for further use. The other method reported by Mohamed⁶¹, after washing the date fruits, was homogenized thoroughly in an electric blender and one liter of deionized water and then centrifuged at 4000 rpm for about 10 min. The supernatant was used without further purification, and the pellets were thrown away. Both these methods yielded the light yellow extract.

3.2 Preparation of leaf extract of *Phoenix Dactylifera* L

The leaves of the *Phoenix Dactylifera* L. were also used for preparing the extract as reported by Aitenneite et al,⁶² Zayed and Eisa,⁶³ Ismail et al.⁶⁴ The leaves after washing with deionized water were soaked in 70% ethanol for 5 minutes. The leaves were dried at 80 °C in the oven to remove moisture content. The dried leaves were crushed in a grinder to powder and even more fine by sieving. The powders were then boiled by taking 2g /100 mL of distilled water. After cooling at room temperature, it was filtered two folds, first by the muslin cloth and then by the Whatman filter paper. Rashid et al⁶⁵ have reported passing the extract through a 0.25 µm syringe filter to obtain super filtered leaf extract. The reddish-brown Date leaves extract were then stored in sterile bottles at 4 °C.

3.3 Preparation of seed extract of *Phoenix Dactylifera* L

The seed extract's preparation was initiated by thoroughly washing the seeds to remove any adhering flesh, dust, and contamination, and then the seeds are air-dried for a day. After drying, two different approaches are found in the literature. Salama et al⁶⁶ and Bouhlali et al⁶⁷ directly grounded the date seeds into a coarse powder using a hammer mill and were further grounded into fine powder by using a heavy-duty grinder. To produce a particle size of 1 mm-2 mm or less, the powders were passed through screens of about 1 mm to about 2 mm. The date seeds were then kept in an airtight container. Whereas the procedures adopted by Khatami and Pourseyedi⁶⁸ and El-Naggar et al⁶⁹ were a bit different. They took around 20g of the simply grind date seeds with 100 mL of deionized water, boiled for few hours under constant stirring. The mixture was then cooled at room temperature and filtered through Whatman filter paper. To be used further as reducing and stabilizing agents, it was kept at 4 °C.

4. Synthesis of Metal Nanoparticles Using Date Parts

The plant-based method for synthesizing metal NPs is dominantly dependent on the phytochemicals in the plant extract. Plant extracts' capability due to their biomolecules and phytochemicals is recognized in the assembly of various well-ordered nanostructures having diversity in sizes and morphologies. In the synthesis of metallic NPs, the biomolecules in the extract have definite roles both as reducing as well as capping/stabilizing agents.^{70, 71} The source of the plant extract influences the typical characteristics of metallic NPs as they may have various concentrations with different

combinations of organic reducing/stabilizing agents. The synthesis of metal nanoparticles using different parts of date palm extract is quite similar to synthesizing other plant extract mediated synthesis. The extracts from the different parts of *Phoenix Dactylifera* L. are mixed with a metal salt solution at room temperature. The reaction is simple and fast as the color change is observed within minutes, indicating the formation of the product. Numerous nanoparticles of the metals such as Ag, Au, Pt, and Cu have been synthesized using the similar procedures^{44, 61, 72-77} with slight variations. It has been established that the amount of synthesized NPs as well their characteristics depends on the metal salt concentration, the pH of the reaction medium, temperature and, the concentration of the extract and its nature.⁷⁸

4.1 Nanoparticles with date fruit extract

The synthesis of silver nanoparticles (AgNPs) using the *Phoenix Dactylifera* L. fruit extract was reported by Farhadi et al.⁴⁴ The author has synthesized spherical silver nanoparticles (AgNPs) with sizes of about 25-60 nm. Silver nitrate treated with date fruit extract showed yellowish-brown color because of the excitation of surface plasmon resonance (SPR) vibrations in AgNPs. The maximum intensity of SPR was observed after 10 min, implying that the reduction of Ag^+ ions to AgNPs is completed. The accountability of this reduction is on the hydroxyl and carboxyl groups in the fruit extract. It was also found that if the fruit extract amount increases, there is a gradual increase of the AgNPs size. The zeta potential with a high negative value of -35mV confirms its expected stability. Further, Zoya Zaheer⁶⁰ too reported the formation of AgNPs by reduction through date fruit extract. The crystalline and spherical shaped AgNPs were having their SRP at 425 nm. They also found that the concentration of the date fruit extract directly influences the shape and position of the SRP spectra as the peaks moved to higher wavelengths with the increase in the concentration of the extract. The produced AgNPs were effective against the series of gram-positive bacteria and exhibited appreciable catalytic activity towards the degradation of NPs.

Shaikh et al⁷³ reported a study of the synthesis of AgNPs having the surface plasmon resonance at 445 nm, and the sizes were between 12-140 nm. The findings again concluded that the phytochemicals, tannins, flavonoids, and proteins are responsible for converting Ag^+ to Ag^0 . The reported AgNPs possessed considerable antioxidant and antimicrobial potentials. Similar results were also obtained by Zafar et al⁵⁷ and Mohammed et al⁷⁴ for the synthesized AgNPs through date fruit extract. Najlaa Al-Radadi⁵⁸ has reported the synthesis of Platinum nanoparticles (PtNPs) by mixing different ratios of the date fruit extract and hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) used as a metal salt. The color change to yellowish-brown was monitored to confirm the formation of PtNPs by reducing platinum from Pt (IV) to Pt (0). As the concentration of platinum salt increased, the SRP peak increased and was found in the range of 321-329 nm. It was also observed that at higher pH, small size NPs were formed and were more efficient in capping the NPs. The XRD pattern further confirmed the crystalline nature and face-centered cubic (*fcc*) structure of the PtNPs. The synthesized PtNPs were also effective against colon carcinoma cells and breast cells and showed considerable antibacterial potential against gram-positive and gram-negative bacteria.

Elwy A. Mohamed reported the Copper nanoparticles (CuNPs) production using the seedless date fruit,⁶¹ by the same reduction method with some modification as cetyltrimethylammonium bromide was added in the stirring Date extract followed by the addition of copper sulfate pentahydrate. The synthesized CuNPs have been confirmed through XRD with crystal faces, and the peaks showed the same pattern as Mustafa Biçer and Ilkay Sisman⁷⁹ for the CuNPs. The FTIR spectrum further affirmed that Cu^{2+} is reduced to Cu^0 because of the carbonyl and hydroxyl groups present in the extract. The CuNPs were spherical, and the SRP emerged at around 560-570 nm. The stability of the synthesized CuNPs was supported with the zeta potential values of +41 mV, and it was due to the capping effect of the phenolic compounds in the date fruit extract.

4.2 Nanoparticles with date seed extract

The study of green synthesis of nanoparticles from the seed extracts of *Phoenix Dactylifera* L. without using the metal was patented by Awad et al,⁸⁰ by mixing the seed powder with 38% hydrochloric acid solution at 1000 rpm speed. The NPs were first isolated through filtration and then by centrifugation. The synthesized date seed NPs were having a size varying between 1-200 nm. These Date NPs were very effective against a variety of bacterial strains responsible for food poisoning. Khatami et al⁶⁸ also reported the date palm seed aqueous extract mediated synthesis of AgNPs by adding varying concentrations of silver nitrate solution to the seed extract resulting in the reduction of Ag^+ to Ag^0 . The spherical shape AgNPs nanocrystals with *fcc* structure confirmed by XRD were produced with the size ranging between 1-40 nm and having a uniform distribution according to the Dynamic Light Scattering (DLS) analysis. The phytochemicals attributed to reducing silver ions to silver in AgNPs are the hydroxyl, carboxyl, and amine groups in the date seed extract. These AgNPs also tend to exhibit antifungal and antibacterial activities. Following the similar synthesis method of AgNPs via date seed extracts were performed by Ansari and Alzohairy,⁸¹ wherein the AgNPs absorption spectra have the SPR peak at 430 nm. The spherical shaped AgNPs produced were having a size between 14-30 nm, supported by DLS measurement of an average diameter of 32.1 nm. These AgNPs were effective against *S. aureus*. Alajmi et al⁸² reported the synthesis of AgNPs through the mixed *Phoenix dactylifera* seeds and *Ziziphus spina-christi* extracts. The synthesized AgNPs were of mixed shape, and the maximum was irregularly shaped, whereas few were spherical with the size ranging between 22.8 -13.2 nm. These AgNPs were further studied as a replacement for the sulfadiazine drug. Mohammadi et al⁸³ synthesized AgNPs through the ethanolic extract of *Phoenix dactylifera* seeds and aqueous silver nitrate (AgNO_3). The formed AgNPs were separated from the mixture via centrifugation at 12000 rpm. FTIR spectrum of the synthesized AgNPs revealed that carbonyl groups and free amine groups in the seed extract bind and stabilize the AgNPs. The absorption spectra band at around 438 nm further confirms the formation of AgNPs. It was also observed that an increase in the seed extract concentration affected the size and the size distribution of the NPs. The XRD analysis shows that the crystallized AgNPs have an *fcc* lattice structure. The XRD further discloses that some metabolite components have crystallized on the AgNPs surface, a strong proof of seed extract components' participation in the synthesized AgNPs. In the spherical-shaped AgNPs, most of them were having a particle size below 19 nm. The authors have also concluded that the AgNPs synthesized by *Phoenix dactylifera* seed extract exhibit strong antioxidant activity because of the capped phenolic groups. Similar methods of synthesis of AgNPs via date seed extract have also been reported by Qidwai et al.⁸⁴

The date seed extract has been used as capping agent for the synthesis of Zinc oxide nanoparticles (ZnO-NPs) was reported by Naggar et al,⁶⁹ wherein, it was shown that the incorporation of *Phoenix dactylifera* seed extract effectively reduces and stabilizes the ZnO-NPs. To shield the *in situ* produced ZnO-NPs from aggregation, it was synthesized on the cotton fabrics. The role of the date seed extract comes into effect as the phytochemicals in it mainly have hydroxyl groups (OH^-), which has a negative charge on the O atom, and it would easily connect with the Zn^{+2} through the ionic-dipolar interaction among the H atom of the phenolic group and O atom of the zinc oxide particles. The spherical shape ZnO-NPs capped with seed extract having a small size reflects its good quality. The DLS analysis exhibited the hydrodynamic size of 97 nm of the ZnO-NPs with a narrow size distribution. The XRD pattern confirms the crystalline nature of the ZnO-NPs. Further, the antibacterial assay evaluation established that ZnO-NPs capped with date seed extract is far superior inhibition than the uncapped ZnO-NPs on the cotton fabrics.

4.3 Nanoparticles with date leaf extract

Most of the nanoparticles derived from the leaf extract of *Phoenix dactylifera* are from silver (Ag) metal. The silver nanoparticles (AgNPs) synthesized from Date leaves extract in a single step have been

reported by Rashid et al.⁶⁵ The reduction of Ag^+ to Ag^0 was observed, varying the concentration of the leaf extract. The absorbance intensity peak appeared within 420-450 nm, and the rise in absorbance intensity was proportional to the leaf extract concentration and led to the decrease in particle size. The FTIR spectrum further corroborated that the phytochemicals in the leaf extract such as proteins, sucrose, flavonoids, and amines were involved as the reducing and capping agents in synthesizing AgNPs as there was an apparent shifting of bands for the phenolic hydroxyl groups, carboxyl groups, and the amines. The XRD studies gave the size of 26.3 nm for the spherical crystallized AgNPs, which is further supported by Scanning Electron Microscopy (SEM), and the size ranges between 30-85 nm. The synthesized AgNPs tested to be an effective antibacterial activity against *E. coli* and *K. pneumoniae* with a potency of 100%. Later on, Aitenneite et al.⁶² proposed the synthesis of AgNPs from leaf extract of *Phoenix dactylifera* but adopting a slightly different methodology. The unique synthetic procedure involves mixing leaf extract and the aqueous silver nitrate solutions and then placing the mixture under microwave exposure for a few minutes. The SPR peaks for the synthesized AgNPs were obtained at 420 nm. The extract's components were responsible for the reduction of Ag^+ and can be justified as the amount of AgNPs produced increases with the increment of extract concentration. The XRD and TEM investigations further revealed the *fcc* structure, and the size of the spherical-shaped AgNPs is about 40 nm. The authors further suggested that the synthesized AgNPs are an effective catalyst for reducing nitro group to amino group for the substituted phenols.

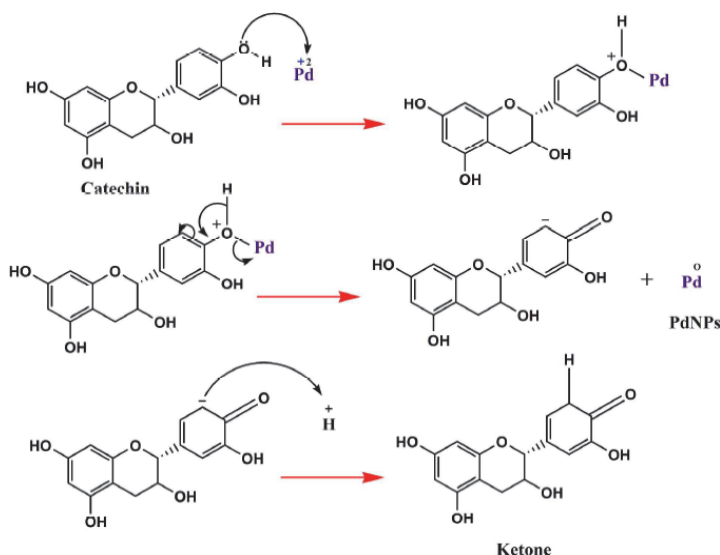


Fig. 3. A mechanism for the reduction and stabilization of PdNPs from leaf extract.⁸⁵

The only work that has been reported to Date in the literature for Palladium nanoparticles (PdNPs) using *Phoenix dactylifera* leaves extract is by Tahir et al.⁸⁵ The synthesis followed the usual procedure using palladium chloride (PdCl_2). Catechin and dactylifric acid from the leaf extract having phenolic groups⁸⁶ were responsible for reducing Pd^{2+} to Pd^0 and stabilizing the synthesized PdNPs. The mechanism of the same has been depicted in **Fig. 3**. The synthesized PdNPs showed the SPR peaks at 278 nm, and the XRD analysis pointed towards the *fcc* crystal structure, whereas the TEM analysis revealed the spherical shape with the average uniform size of 2-5 nm. The size and shape of different NPs synthesized through date extract are represented in **Table 2**. The synthesized AgNPs were having good antibacterial and catalytic activities. The synthesis of gold nanoparticles (AuNPs) with date leaves extract by adding the extract with aqueous tetrachloroauric acid solution at room temperature has been reported by Zayed and Eisa.⁶³ The spherical shaped AuNPs with the size ranging between 32-45 nm were confirmed by TEM analysis. The stabilization of the AuNPs was made possible by the interactions of the $-\text{OH}$ and $-\text{CO}$ groups present in the phytochemicals such as flavonoids, phenolic acids, and tannins in the leaves extract of *Phoenix dactylifera*. The spike in absorption peak was determined at

552 nm as more AuNPs were formed due to the reduction of Au^{3+} ions. TEM analysis further clarified that the spherical shaped AuNPs are sized between 32–45 nm. Further studies on the catalytic behavior of AuNPs demonstrated that they are size-dependent towards the degradation of nitrophenol to aminophenol.

5. Characterization of Nanoparticles of Phoenix Dactylifera L.

Usually, the synthesized NPs are analyzed for their morphological features as the properties of the NPs are influenced by their morphology and the structural features that signify the nature and composition of the NPs. The standard characterization techniques that are generally used for analyzing both these properties are UV-Visible spectroscopy, Fourier transform infrared (FTIR) spectroscopy, Dynamic light scattering (DLS), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), and X-ray diffraction (XRD).

5.1 UV-visible spectroscopy

The characterization by UV-Visible spectroscopy is based on the basic light principles known as the Beer-Lambert law. The synthesis of NPs from their respective salts of the Ag, Au, Pt, Pd, Cu, or Zn is monitored through UV-Vis spectroscopy as they give their characteristic peaks at different absorptions. The absorbance of the nanoparticle samples at light wavelengths ranging from 300–800 nm and their sizes in between 1–100 nm is frequently used to confirm nanoparticles' synthesis.⁸⁷ The strong absorption band known as surface plasmon resonance (SPR) is shown only in the spectrum of metal NPs, not in the spectra of metal solutions.⁸⁸ The AgNPs possess absorption peaks in the range of 400–450 nm, whereas the AuNPs have it at around 500–550 nm. The UV-vis intensity and absorptions are influenced by the NPs shape and size. It is the primary technique employed by many authors^{89, 90} for the stability and formation of metallic NPs. The absorption peaks in the UV-Vis spectra for PdNPs are usually below 300 nm.⁹¹ PtNPs usually have their maximum absorption between 300–350 nm. At higher concentrations, it may present a small redshift. An increase in the concentration of the date extract, or the reaction time, a gradual increase in the absorption peaks indicates the formation of NPs. The green synthesized metallic NPs frequently exhibit surface plasmon resonance (SPR) that helps in the absorption in the UV-Visible region. Researchers have determined that ZnO nanoparticles with date extracts displayed broad peaks in the visible region and an intense peak in the UV region employing UV-Visible spectroscopy.

5.2 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a powerful surface chemical analytical tool for characterization. The nature of the organic functional groups such as carbonyls, hydroxyl, or any other required group is attached to the NPs surface can be evaluated through FTIR.⁹² FTIR analysis is carried out to detect the surface capping and purity of the formed NPs and is measured from 250–4000 cm^{-1} . The common approach is comparing the FTIR spectrum of the date extract before synthesis with that of the NPs synthesized with it is made that gives vital data of the functional groups involved in the reduction and stabilization. The prominent functional groups show phenolic O–H, amide NH, C=O, C–OH stretching bands. They may be present in carbohydrates, flavonoids, terpenoids, proteins, and phenolic compounds and are responsible for reducing metal ions, paving the way for the synthesis of NPs. In work reported by Al-Radadi,⁵⁸ the combining of phytochemicals with PtNPs was shown by shifting of -NH frequency of the amino acid group from 2900 cm^{-1} to 2790 cm^{-1} .

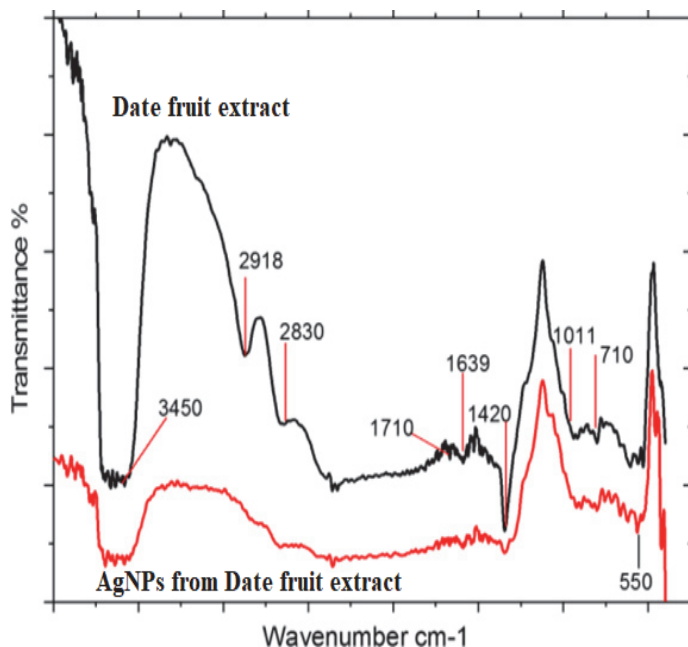


Fig. 4. FT-IR spectra of Date fruit extract and AgNPs from Date fruit extract.⁵⁷

5.3 Dynamic light scattering (DLS)

Dynamic light scattering (DLS) is one of the techniques to estimate the size of the NPs and is also used to characterize the surface charge and the size distribution of the particles.⁹³ In DLS, particles' hydrodynamic size is measured by analyzing the scattered light intensity modulation as a function of time.⁹⁴ The DLS technique's advantages is that it is a table top instrument that is easy to operate, fast, sensitive, and selective to size and concentration changes of the NPs. Additionally, the NPs with high molecular mass are also analyzed and do not require calibration. However, the disadvantage with the DLS technique is that it can measure the size of the monodispersed NPs even at a very low level. Still, it is not accurate in measuring polydisperse nanoparticles with large size.⁹⁵ DLS also measures the zeta potential, which is the charge acquired by particles in the solution, and it indicates the stability of the nanoparticles. The average particle size of the NPs obtained from DLS is typically larger than those obtained from microscopic techniques. It measures all the substances adsorbed on NPs surface and not only the metallic core. A study by Tahir et al⁸⁵ has observed that the particle size distribution of the PdNPs synthesized from date leaf extract ranged from 5-18 nm. Another survey by Ansari and Alzohairy⁸¹ indicated the average diameter of 32.1 nm, whereas Khatami and Pourseyedi⁶⁸ have reported the average size of 27 nm for the AgNPs synthesized from date seed extract. The hydrodynamic diameter of the synthesized CuNPs reported by Mohamed⁶¹ was approximately 78 nm, as shown in **Fig. 5**. All the size analyzed for the *Phoenix dactylifera* mediated synthesis of NPs falls within the stipulated range for establishing the nanomaterials.

5.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a versatile, high-resolution imaging technique that delivers insight into the morphology, topology, and surface characteristic of the fabricated NPs. Based on the electron scanning principle, SEM determines the NPs shapes, sizes, distribution, and the dispersion of nanoparticles in bulk at the nanoscale level. SEM's main advantage is that it determines the morphology of NPs smaller than 10 nm but is not useful in determining its internal structure.⁹⁶ From the SEM study, Tahir et al⁸⁵ have confirmed that most of the PdNPs synthesized by Date leaves extract are spherical and have a uniform distribution, and the PdNPs are well dispersed. A similar analysis using SEM was reported by Qidwai et al⁸⁴ for AgNPs from date seed extract revealing mostly the spherical shape without any agglomeration. In another study of NPs with *Phoenix dactylifera* fruit extract, Ezhilarasi

et al⁹⁷ reported the rod-shaped surface of well-dispersed NPs having little agglomeration. The interesting feature from the literature report^{58, 63, 65, 98, 99} reveals that the morphology of almost 99 % of the nanoparticles derived using extracts from different parts of *Phoenix dactylifera* is spherical.

5.5 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is the general analytical tool that is crucial for determining the size of nanoparticles and the size distribution and morphology. TEM can deliver data even from low to high magnifications and can scan particles in a wide size range. Because of the continuous demand to visualize the lattice arrangements in the crystalline NPs, it has to generate high atomic resolution images. This considerable enhancement of TEM power is possible by integrating many sophisticated techniques, and one such advancement is high-resolution TEM. The resolution of TEM is a thousand times higher and has enhanced effectiveness in terms of three-dimensional resolution in comparison to SEM.¹⁰⁰ But the limitation with the TEM technique is that it gives low magnification if the particle size is less than 100 nm. Farhadi et al⁴⁴ noticed the date extract synthesized AgNPs are spherical with a size ranging from 25-60 nm, whereas a similar study by Zafar and Zafar⁵⁷ reported the size between 20-100 nm through TEM. Using the TEM images, Al-Radadi⁵⁸ observed the variation in size of PtNPs at different pH conditions.

Table 2. Synthesis of NPs from date extract

Type of NPs	Parts extracted	Size (nm)	Shape	Characterization	Application	Ref.
Pt	Fruit	1.3-2.6	Spherical	UV-vis, FTIR, XRD, TEM, EDX, TGA	Anticancer, Antibacterial	58
Ni	Fruit	32±5	Rod-shaped	UV-vis, FTIR, XRD, TEM, Photoluminescence spectroscopy	Antibacterial, Photocatalytic degradation	97
Ag	Fruit	25-60	Spherical	UV-vis, FTIR, XRD, SEM, TEM, EDX	Antibacterial, Catalytic	44
Ag	Fruit	--	--	UV-vis	Antioxidant, Antibacterial	59
Ag	Fruit	12.2-140.2	Spherical	UV-vis, SEM, EDX	Antioxidant, Antimicrobial	73
Ag	Fruit	20-100	Spherical	UV-vis, FTIR, TEM	Antimicrobial, Cytotoxicity	57
Ag	Fruit	20-60	Spherical	UV-vis, FTIR, SEM, TEM, DLS	Antibacterial, Anticancer	74
Cu	Fruit	78	Spherical	UV-vis, FTIR, TEM, DLS, XRD	--	61
Ag	Fruit	3-30	Spherical	UV-vis, SEM, TEM, DLS, EDX	Catalytic, Antimicrobial, Optical	60
Ag	Seed	14-30	Spherical	UV-vis, SEM, TEM, DLS	Bactericidal	71
Ag	Seed	17-19	Spherical	UV-vis, FTIR, SEM, TEM, XRD	Antioxidant, Anticancer	83
Ag	Seed	1-40	Spherical	UV-vis, XRD TEM, DLS	Antibacterial, Antifungal	68
Ag	Seed	13.2-22.8	Irregular	UV-vis, SEM TEM, DLS	Anti-toxoplasma activity	82
ZnO	Seed	97nm	Spherical	TEM, SEM, XRD, EDX	Antibacterial	69
Ag	Leaf	30-85	Spherical	UV-vis, FTIR, SEM, XRD,	Bactericidal	65
Pd	Leaf	5-21	Spherical	UV-vis, FTIR, SEM, TEM, XRD, DLS, EDX	Antioxidant, Antibacterial, Hemolytic, Catalytic	85
Ag	Leaf	20-60	Spherical	UV-vis, TEM, XRD	Catalytic	62
Au	Leaf	32-45	Spherical	UV-vis, FTIR, TEM	Catalytic	63
Ag	Root Hair	15-41	Spherical	UV-vis, FTIR, TEM, SEM, XRD, EDX	Anticancer, Antibacterial	98
Au	Pollen	95	Spherical	UV-vis, SEM, EDX	Anticancer	99
Ag	Pollen	27	Spherical	UV-vis, SEM, EDX	Anticancer	99

5.6 X-ray diffraction (XRD)

The X-ray diffraction (XRD) is a crucial technology to determine the structural information phase identification about the crystalline form of metallic NPs. Strong X-rays can penetrate materials deeply and gives data on the bulk structure.¹⁰¹ The widening of the peaks in the XRD endorses the fabrication of nano-sized particles. The crystal structure explains the atoms' arrangement, position, and power of diffraction peaks. The XRD technique can identify the nanoparticles in single as well as in multiple

phases. The XRD is a simple, very delicate, easy to use, and non-destructive technology. The main reason for using this technique for determining the structure of NPs is because the X-rays measure the wavelength on an atomic scale. The operation of XRD is based on Bragg's law.¹⁰² The Debye-Scherrer equation is applied to determine the crystalline size of the NPs from the XRD data. The Bragg reflection is calculated through the formula:

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

(where d is the crystalline size of the NPs in nm, K is the Scherrer constant, λ is the wavelength of X-ray radiation, β is the angular full width at half maximum, and θ is the diffraction angle).¹⁰³ However, for small nanoparticles that are less than hundreds of atoms in size, it isn't easy to obtain the structural and additional parameters with their precise dimensions. Al-Radadi⁵⁸ has used the XRD spectra to ascertain the crystallinity of PtNPs synthesized from *Phoenix dactylifera* fruit extract, and the pattern shows an index plane for dissimilar values of 2θ . The Bragg's reflection identified at 2θ values of 39.38, 45.88, and 67.33° correspond to the index plane of 1 1 1, 2 0 0 and 2 2 0, respectively, which is the characteristic feature of *fcc* structure as shown in **Figure 5**. The synthesis of CuNPs was well established by Mohamed⁶¹ that exhibited peaks at angle 43.27, 50.41, and 74.17° corresponding to 1 1 1, 2 0 0, and 2 2 0 Bragg's plane inferring that the copper crystallites have *fcc* lattices.

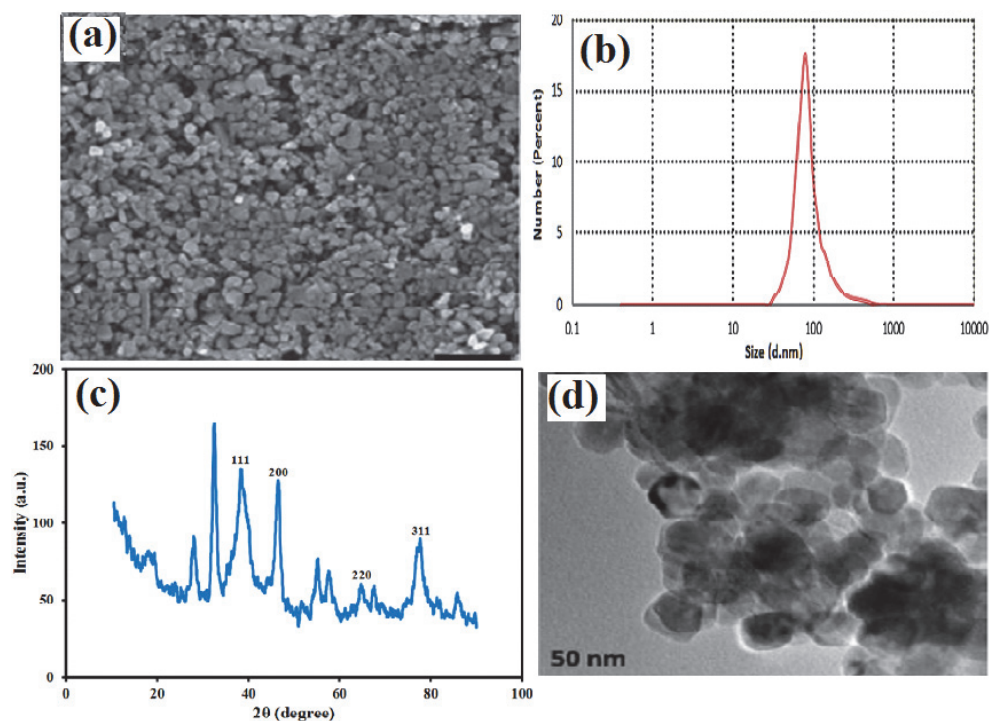


Fig. 5. (a) SEM of AgNPs from seed extract⁸³ (b) DLS of CuNPs from fruit showing Particle Size Distribution⁶¹ (c) XRD of AgNPs from leaves⁶⁵ (d) TEM of AgNPs using fruit extract.⁵⁷

6. Application of Nanoparticles and Future Perspectives

The *Phoenix dactylifera* L. mediated nanoparticles' synthesis is gradually gaining popularity among scientists because of appreciable properties such as economical, non-hazardous, significantly soluble in water, biocompatible, and lack toxic stabilizers. Therefore, the green synthesis route provides ease and extra benefits towards biomedical application. These nanoparticles find their use in different biomedical applications due to their higher surface to volume ratio and some explicit properties. As the green synthesized NPs are expanding in biomedicine, special attention is given towards their cytotoxicity to determine appropriate strategies for the assessment, communication, and management of NPs to safeguard human health besides the environment. The influence of cytotoxicity studied concerning the fabricated NiO nanoparticles towards A549 cell lines exhibited excellent outcome.⁹⁷

Reactive oxidizing species oxidizes the protein and lipids resulting in toxic electrophiles toxicity to wrong pathways of cellular signal transduction. The NiO NPs synthesized through *Phoenix dactylifera* L. extract induces cytotoxicity. It possesses the ability to release metal ions and additional features such as impeccable morphology and definite surface area, enabling them to participate in cellular activities. The suitability of AuNPs and AgNPs for application in the medical field is due to their biocompatible nature and great affinities towards biological molecules like lipids, proteins, antibodies, or even microorganisms such as bacteria and viruses.¹⁰⁴ When these AgNPs/AuNPs are functionalized with biomolecules facilitates them as biomarkers for drug delivery and finding of disease.¹⁰⁵ *Phoenix dactylifera* L. seeds have a high capacity in forming AgNPs from AgNO₃ solution. Therefore, they are utilized as a bioreactor for manufacturing AgNPs at the industrial level, with remarkable properties like highly stable, enhanced antibacterial and antifungal activity, low cost, and environmental compatibility. These properties empower the AgNPs with higher effectiveness as compared with conventional drugs like colistin and polymyxin.⁶⁸ In general, the AgNPs/AuNPs have exhibited broad-spectrum antibiotic action against microbes. The charismatic feature of the AuNPs from leaf extract of *Phoenix dactylifera* L. is that it is feasible to tune its size within the nanoscale, which shows size-dependent catalytic activity. Hence, these AuNPs are frequently used for the degradation of 4-nitrophenol to 4-aminophenol.⁶³ The synthesized AgNPs from date fruit extract can be potentially used for antioxidant activity. This high antioxidant potential is attributed to the high amount of polyphenolic compounds in date extract. Various researches have also emphasized that the AgNPs from date fruits extract show convincing antimicrobial results against gram-positive and gram-negative bacteria such as *E. coli*, *S. aureus*, *K. pneumoniae*, and *C. albicans*,^{65, 73} and there is no report to Date on its resistance. PtNPs from Date extracts has shown encouraging outcomes as an anticancer agent. They were successful to a considerable extent in obstructing the growth of human cancer cells such as hepatocellular carcinoma cells (HepG-2), colon carcinoma cells (HCT-116), and breast cancer cells (MCF-7). Henceforth, PtNPs find their application as an economical substitute for the treatment of cancer.⁵⁸ In addition to antimicrobial and catalytic activity, PdNPs formed from the date leaf extract actively scavenged DPPH free radicals, making the water purification easier and cheaper.⁸⁵

Investigations have shown that the date extracts have the effective antioxidant and mutagenic activity at a slightly higher level than the extract of other plants.^{106, 107} The antioxidant activity is credited to the comprehensive range of a phenolic compound in dates including p-coumaric, ferulic, and sinapic acids, flavonoids and procyanidins as well as the presence of vitamin C.¹⁰⁸ The concentration and composition of phenolic acids, isoflavones, lignans, and flavonoids, tannins, and sterols varies depending on conditions such as the variety of dates, the geographical origin, and soil type, but are comparable with any other plant extracts that are generally used in green synthesis of NPs.^{48,109} For example, the concentration of carotenoid in fruit extract of dates (0.97 mg/100 g) is higher than that of the figs (0.032 mg/100 g).⁴⁸ Many researchers have reported^{50,110,111} that the number of phenolic acids in Date extracts are significantly higher than the other plants. However, we could not find any comprehensive report or review comparing the advantages that date extracts have over other plant extracts to synthesize NPs. In the last decade, green synthesized nanoparticles from *Phoenix dactylifera* L. have played a considerable role in developing the pharmaceutical field. It unfolds a new perception owing to its anticancer and antimicrobial properties. In the future, these NPs might be used for tumor therapy, depending on their adjustable size, toxicity, and biocompatibility. The antioxidant feature can give them a significant place in the nutraceutical and food industries. Unexpectedly, less work has been reported in the literature either of the synthesis or application of NPs from dates. Regardless of the potential advantages of green NPs in biosensors, their application is marginal and so far has not made its impact compared with other applications of NPs from Date. Nevertheless, these NPs have therapeutic and diagnostic applications in the medical field for humans, but no research has been carried out probing their application in veterinary medicine. At the pace at which the applications of NPs from dates are investigated, it is obvious that it may influence the global consumption of NPs products derived from date palms in the near future. Therefore, avenues are open for the researchers to

design new strategies or routes for synthesizing NPs from dates that may find application in the veterinary field.

7. Conclusion

In the last two decades, the green synthesis of metallic NPs has gathered considerable scientific community response. The present work emphasizes nanoparticles' synthesis using extracts from various parts of the *Phoenix dactylifera* L. plant. The extraction methodologies, the synthetic strategies, the characterization techniques involving UV-Vis, FTIR, DLS, SEM, TEM, and XRD and their applications have been discussed in detail. Date seeds, leaves, or fruits used as a green source played a dual role as reducing and stabilizing agent with immense potential to produce numerous NPs with metal or metal oxides like Ag, Au, Pt, Pd, Cu, CuO, and ZnO. The different synthetic routes discussed in this review were useful for fabricating particles in the nano range and were dependent on the conditions such as pH, temperature, and concentration of the extract.

Additionally, all the synthesis was a single step process and found to be more eco-friendly, economical, non-toxic, less time consuming, and benign. The date extracts containing phytochemicals such as flavonoids, alkaloids, carotenoids, polyphenols, etc., were responsible for the NPs synthesis. A little discrepancy in *Phoenix dactylifera* L. extract's chemical composition was observed in sample collection from different regions. Still, it does not induce any striking differencing in their reducing, capping, or stabilizing effect. It can be inferred from the studies that the application of these NPs are impacted by their size, shape, or surface area, and they have prospective applications in catalytic and biomedical fields, but the researchers are more concentrated on their antibacterial and anticancer activities. Continued research needs to be carried out to make the date extract mediated NPs the leading NPs of the future.

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