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Sustainable Preparation of Graphene Quantum Dots from Leaves of Date Palm Tree

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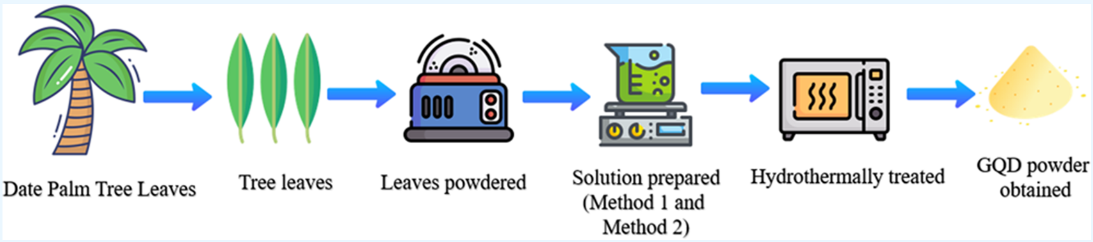

ABSTRACT: The date palm (*Phoenix dactylifera*), a subtropical and tropical tree, included in the family *Palmae* (*Arecaceae*) is one of the oldest cultivated plants of mankind. Date palm is a major agricultural product in the semi-arid and arid areas of the world, particularly in Arab countries. These trees generate high quantities of agricultural waste in the form of dry leaves, seeds, etc. In this study, dried date palm leaves were used as green precursors for synthesizing graphene quantum dots (GQDs). This work reported the preparation of GQDs using two different sustainable methods. GQD-1 was developed using a simple, hydrothermal technique at 200 °C for 12 h in water, with no requirement of reducing or passivizing agents or organic solvents. GQD-2 was prepared using a hydrothermal technique at 200 °C for 12 h in water, with the usage of just distilled water and absolute ethanol. The compositional analysis of the leaf extract was performed, along with the morphological, compositional, and optical examination of the sustainably developed GQDs. The characterization results confirmed the successful formation of GQDs, with average sizes ranging from 3.5 to 8 nm. This study helps to obtain GQDs in an economical, eco-friendly, and biocompatible manner and can assist in large-scale production and in recycling date palm tree waste products from Middle East countries into value-added products.

1. INTRODUCTION

Date palm is a major agricultural product in the arid as well as semi-arid regions of the world, particularly in the Middle East and North Africa.[1] There are approx. 120 million date palm trees globally, producing millions of tons of dates each year, in addition to secondary products such as palm midribs, fronds, stems, leaves, and coir.[2] In Arab nations, there are over 85 million cultivated date palm trees with the majority in Saudi Arabia, United Arab Emirates, Tunisia, Morocco, Algeria, Iran, Iraq, and Egypt.[3] In the Arabian Peninsula, it has played a significant role in the daily life of the people for the past 7000 years. In the Kingdom of Saudi Arabia, the most recent statistics stated that the number of palm trees goes beyond 28 million in 160,000 hectares, indicating that about 55% of the total domestic production of date palm fruit is produced by nearly 120,000 farms.[4] Conversely, the local agriculture sector produces almost 1700 million tons each year of date palm tree wastes as well as agricultural products. Several studies have stated that the Kingdom of Saudi Arabia alone produces more than 200,000 tons of date palm biomass each year.[5,6] As per an estimate, each date tree makes almost 20 kg of dry leaves every year.[7] It is the main fruit tree cultivated in Qatar, and the date production is 7.20% of the entire agricultural production.[8] The local farms in Qatar produce large quantities of date palm tree byproducts (stems, pods, leaflets, fruit bunch, etc.), which cannot lead to benefits. Date palm is regarded as a renewable natural resource due to the fact that it could be substituted in a comparatively short time period.[9−11] After planting, it takes 4 to 8 years for date palm trees to bear fruit and 7 to 10 years to generate sustainable yields for commercial harvest.[12,13] Typically, date palm wastes can be burned in farms or can be disposed of in landfills, which results in environmental contamination in date-producing nations.[11,14,15] The main constituents of date palm biomass include lignin, hemicelluloses, and cellulose.[16,17] Furthermore, date palm has low moisture content and high volatile solids content.[15,18] These factors make date biomass an excellent waste-to-energy resource in the MENA region. Increasing customer needs, environmental deterioration, and energy crisis have forced

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researchers to search for green, inexpensive, and facile routes to produce innovative and advanced materials using renewable resources. The research interest of scientists in developing environmentally friendly materials has enhanced significantly within the past 20 years, and in this context, date palm wastes can be considered a useful biomass resource.

Nanomaterials have experienced significant growth in recent times, and we are witnessing a large number of applications for nanostructured materials in various fields.[19−21] A graphene quantum dot (GQD) is a material with zero dimension in the family of carbon nanomaterials and is usually regarded as a shredded portion from a graphene sheet.[22,23] The GQD material is investigated extensively ever since its unexpected discovery in the year 2004, at the time of the purification of carbon nanotubes.[24] This material has a honeycomb structure possessing a single carbon layer,[25] and it has been extensively explored recently because of its exceptional structure-related properties, like electrical, optical, and optoelectrical properties. GQDs are an advanced type of quantum dots (QDs), as these materials have good physical and chemical stability, due to their intrinsic inert carbon property.[26,27] In addition, GQDs are very eco-friendly materials because of their nontoxicity and biologically inert properties, which have drawn universal interest from industry as well as academic sectors. GQDs have excellent chemical, structural, electrical, and adjustable optical characteristics of photoluminescence and electrochemiluminescence. The improved stability, nontoxicity, good solubility, superior dispersibility, biocompatibility, and inertness of this material facilitate its vast possibility in numerous uses.[28,29] In general, nanomaterials have huge scope of application in desalination, water treatment, and other environmental remediation applications.[30−34] However, it can be noted that the research on GQDs is still in a preliminary phase, and several challenges of GQDs have yet to be addressed. To meet the industrial demands, it is essential to mass produce GQDs at a comparatively low cost.

Different synthesis methods have been employed for the GQD preparation, which could be classified into two types (i) top-down and (ii) bottom-up approaches. The top-down approach necessitates the breakdown of bulk materials to minute-sized nanomaterials. On the other hand, the bottom-up approach involves the development of larger units from small units, and it includes techniques such as hydrothermal heating, microwave irradiation, thermal combustion, and cage-opening technique. Although the above-stated techniques have numerous advantages, these approaches need complicated purification methods and superior quality carbon precursors and involve treatment with concentrated acid or alkali, elevated temperature, low quantum yield, and harmful organic solvents. Naturally occurring carbonaceous materials have received substantial research consideration globally due to their excellent physical characteristics and chemical properties, unique morphologies, and outstanding applications. Although various carbon species such as coal,[35] carbon fibers,[36] carbon black,[37] etc., could be employed as precursors for GQD synthesis, GQDs are also related to fossil fuels, a nonrenewable resource that would not be sufficiently available in the future.[38,39] Practically, the GQD preparation must not adversely impact the surroundings, as generally harsh conditions with strong acids have been employed for its preparation. Moreover, electrochemical methods for GQD preparation are noted to have low quantum yield (QY).[40,41] All of the above-stated findings are motivating the researchers to investigate techniques to develop GQDs from inexpensive, natural, sustainable, and renewable precursors like green plants. Therefore, green chemistry approaches have been employed in recent times for nanomaterial synthesis, which offer extra benefits like the opportunity of recycling the waste products into valuable products, commercial production possibility, massive availability of diverse carbon sources, unique morphologies, biocompatibility, environmentally friendly synthesis approaches, and economic nature.[42,43] The sustainably prepared GQDs from different carbon sources like flower extract,[44] tea waste,[39] mango leaves,[45] etc., are already stated. The results obtained from the above-stated research works motivated us for the research whether we can develop GQDs from renewable, inexpensive, natural, and sustainable sources like green plants, which are the basis of most of the world's ecologies. A few studies were also carried out to develop GQDs from Eucalyptus tree leaves and Banyan tree leaves.[46−48] Certain polysaccharides, proteins, biomolecules, and enzymes in plants possess a great ability to carry out reduction and capping of nonbiocompatible materials. Plant-derived materials have been noted to be an excellent source for the green synthesis of carbon-based nanomaterials, as these materials have increased carbon amounts to synthesize the carbon nanostructured materials.[49,50]

Therefore, in our study, two methods are used to prepare GQDs from date palm leaves in a very sustainable and eco-friendly way. This is the initial attempt to synthesize GQDs from date palm tree leaves. The dried date palm leaves are used as green precursors for synthesizing GQDs. The green fabrication of the GQDs from biodegradable agri-based byproducts is very beneficial considering its eco-friendly nature and sustainability. This study will develop the finest application of locally approachable date palm tree byproducts, to make them an important and valuable material for different applications. Aitenneite et al.[51] put forward a quick as well as environmentally friendly green microwave-assisted preparation of silver nanoparticles from silver nitrate solution utilizing aqueous *Phoenix dactylifera L.* leaf extract. In a research work carried out by Khatami et al.,[52] biological synthesis of silver nanoparticles was performed using date palm pit aqueous extract. Mohiuddin et al.[53] studied the carbon nanoparticles that were multicolored, had biocompatibility, and were pulled from date palm fronds. The characterization results demonstrated that the carbon-based nanoparticles were crystalline graphitic as well as hydrophilic in nature with sizes in the range of 4−20 nm. Farhadi et al.[54] prepared spherical silver nanoparticles by an eco-friendly, simple, rapid, and low-cost method employing date palm fruit extract as a natural and advanced reducing and stabilizing agent.

Hence, the current study presents the preparation of value-added materials from the local environmental biomass. The GQDs are prepared from the date palm leaf powder, as per the current study, by using two sustainable preparation methods. The first method employs the utilization of just distilled water without using any chemicals during its synthesis. A facile, hydrothermal method is employed with heating of solution at 200 °C for 12 h in water, with no requirement of reducing or passivizing agents or organic solvents, and the GQDs obtained are termed "GQD-1." The second method involves the use of distilled water and absolute ethanol for the GQD synthesis, and the GQDs developed can be termed "GQD-2." The ethanol used during the GQD-2 synthesis is removed eventually during the process, thereby making it a sustainable

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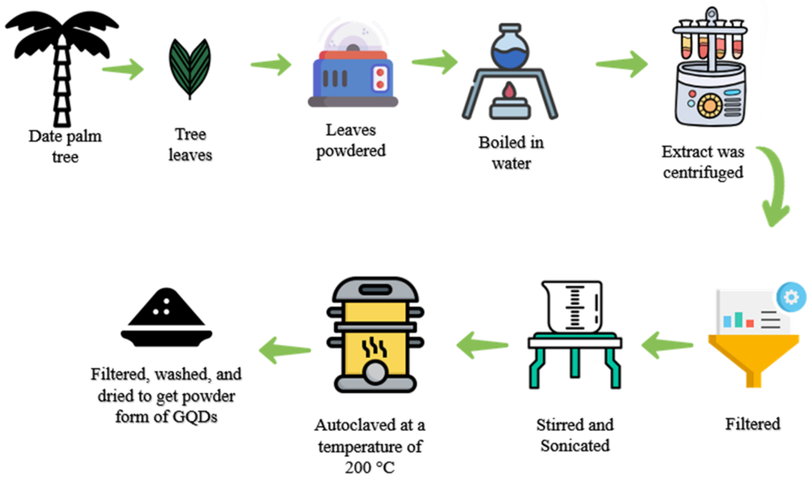

Figure 1. Schematic representation of preparation of GQDs from date palm leaves as per method 1.

process. To the best of our knowledge, this is the first attempt at preparing GQDs from date palm tree leaves. The dried date palm leaves are used as green precursors for synthesizing GQDs. The green fabrication of the GQDs from biodegradable agri-based byproducts is very beneficial considering its eco-friendly nature and sustainability. This study will develop the finest application of locally approachable date palm tree byproducts, to make them an important and valuable material for different applications. The synthesized GQDs are characterized using transmission electron microscopy (TEM), Fourier transform infrared (FTIR), Raman, ultraviolet−visible (UV) spectroscopy, and photoluminescence (PL) spectroscopy. As the GQDs in this study are prepared from metal-free precursors, these materials have the minimum probability of cellular toxicity and do not need extra capping or passivation to make these materials stable and biocompatible. Thus, the study helps to obtain GQDs in an economical, eco-friendly, and biocompatible manner and can help in large-scale production and in recycling date palm tree waste products from Middle East countries into value-added products.

2. EXPERIMENTAL SECTION

2.1. Materials and Apparatus. Date palm tree leaves were taken from the date palm tree in Qatar University, Qatar. The ethanol used in the work was obtained from Sigma-Aldrich. Distilled water used was attained from Merck. A high-temperature autoclave with poly(tetrafluoroethylene) (PTFE) lining was purchased from Techinstro. This hydrothermal autoclave reactor was used to perform a hydrothermal reaction at elevated pressure as well as increased temperature up to 200 °C maximum. This reactor was mostly made up of two parts: an inner Teflon liner or Teflon chamber and an outer high-quality stainless steel jacket. The universal oven used was the Memmert UNE series, Type UFB 400. The stirring hot plate with a digital display employed was a Corning PC-420D. A Mettler Toledo XS105 weighing balance was employed. The benchtop centrifuge Sigma 2-16P used was from SIGMA (Germany). The planetary ball mill PM 100 used was purchased from Retsch.

2.2. GQD Preparation from Dry Leaves of Date Palm Tree Using Deionized Water. In the first method, fresh date palm leaves were collected, and then all of the surface impurities were removed. Then, the leaves were heated in an oven at 105 °C temperature for 8 h for drying the leaves properly. Subsequently, the leaves were cut into small pieces for further mechanical treatment. These cut leaves were ball-milled for 30 min for getting fine leaf powder. About 5 g of ball-milled date palm leaf powder underwent heating in 200 mL of deionized water at a temperature of 80 °C for 1 h. To separate the solid remains, the solution was centrifuged at an RCF of 10,000*g* for 10 min. After the centrifugation, the supernatant was collected and subsequently filtered, and the obtained solution was stirred as well as sonicated for 30 min. Then, it was kept in an autoclave and heated at 200 °C for 12 h for hydrothermal heating. After the specific time, the autoclave was taken out and the solution was collected. The precipitate from the obtained solution was discarded and the remaining solution was filtered several times, subsequently washed, and then dried at 70 °C for 4 h to obtain the GQD powder. These GQDs obtained from the leaves of date palm tree using this very sustainable method was termed "GQD-1." Here, GQDs are prepared by employing just the tree leaf powder and the deionized (DI) water, without the requirement of any chemicals. The schematic representation for the synthesis of graphene quantum dots from date palm tree leaves as per method 1 is termed GQD-1 and is shown in Figure 1.

2.3. GQD Synthesis from Dry Leaves of Date Palm Tree Using Ethanol. The second method involves collecting fresh date palm leaves and removing surface impurities, and then 10 g of date palm leaves were cut into small pieces (almost 1 to 2.0 cm) and dipped in a solution of pure ethanol. Subsequently, this solution was stirred for 4 h at room temperature. The resulting extract was undergone centrifugation at 8000 rpm for 10 min to achieve a fine supernatant. Furthermore, the acquired extract was filtered employing a 0.22 μm filter and subsequently concentrated by evaporating ethanol with the help of a rotary evaporator till the excess slurry was achieved. The slurry was combined with a low quantity of distilled water and then undergone heating at 200 °C for 12 h in an oven, and subsequently the residue was undergone dispersion in absolute ethanol to disperse the graphene quantum dots well. The attained dispersion was subsequently filtered out employing a syringe filter to obtain GQDs. Then, the GQD solution was filtered and dried correctly. These GQDs obtained from the leaves of date palm trees using this method 2 were termed "GQD-2." Here, GQDs are prepared by employing just the tree leaf powder, DI water, and ethanol, without the requirement of any other chemicals.

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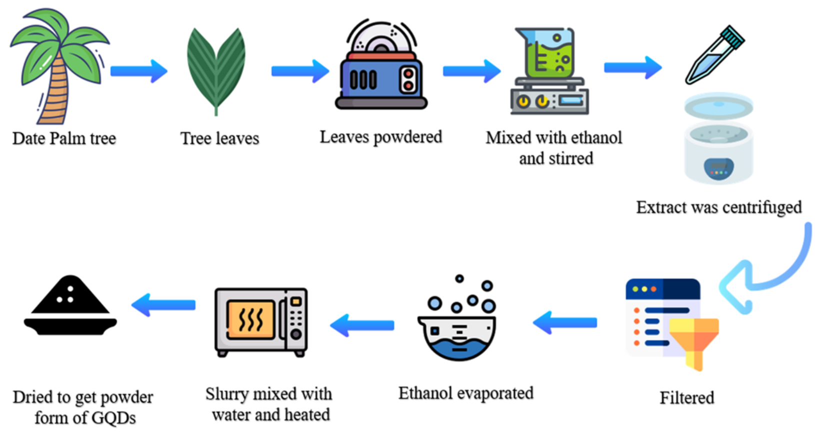

Figure 2. Schematic representation of preparation of GQDs from date palm leaves as per method 2.

The schematic representation for the synthesis of graphene quantum dots from date palm tree leaves as per method 2 is termed GQD-2 and is shown in Figure 2.

2.4. Characterization of the Prepared GQDs. The optical properties of GQD-1 and GQD-2 were analyzed using a Biochrom UV−vis absorption spectrophotometer. Photoluminescence (PL) characteristics of GQD-1 and GQD-2 were analyzed using a FluoroMax-4 Spectrofluorometer—Horiba, the fluorescence spectrophotometer. GQDs illustrate tunable PL through the manipulation of edge functionality under distinct preparation conditions. In the current study, the FTIR instrument employed was 760 Nicolet, and it helped in the detection of organic as well as inorganic groups present in the GQD samples, in accordance with their particular IR frequency. The morphologic characteristics of GQD samples were analyzed using transmission electron microscopy (HT 770, Hitachi, Japan). The instrument employed for Raman spectroscopy was a Thermo Fisher Scientific DXR Raman microscope having a wavelength of 532 nm, 40 times scanning, and a laser power of 0.1−10 mW using 50× microscope objectives. Furthermore, the presence of GQDs was clearly confirmed by the peaks noted from the Fourier transform infrared spectroscopy (FTIR) analysis. The FTIR instrument employed for the GQD analysis, in this study, was a 760 Nicolet FTIR model. NMR analysis for the two samples for ^{1}H spectra and ^{13}C was carried out using a JOEL NMR 600 MHz.

2.5. Product Yield of the Graphene Quantum Dots Developed. The product yields of GQD-1 and GQD-2 synthesized were established using eq 1.

$$\text{yield (\%)} = \frac{\text{weight of dried GQD obtained}}{\text{weight of slurry}} \times 100 \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. Leaf Extract Characterization. In the subsequent section, the results of the compositional analysis of the date palm tree leaf extract are presented. FTIR analysis was carried out to examine the leaf extract composition and the result is shown in Figure 3. The FTIR spectrum of date palm leaf extract showed a broad peak at 3367 cm^{-1} that can be associated with the stretching vibration of −OH groups of polyphenolic and phenolic constituents available in the date palm leaf extract. Additional peaks were noted at 2800−3000 cm^{-1}, which can be because of the stretching vibrations of C−H of aromatic skeletons such as aromatic acids and flavonoids.

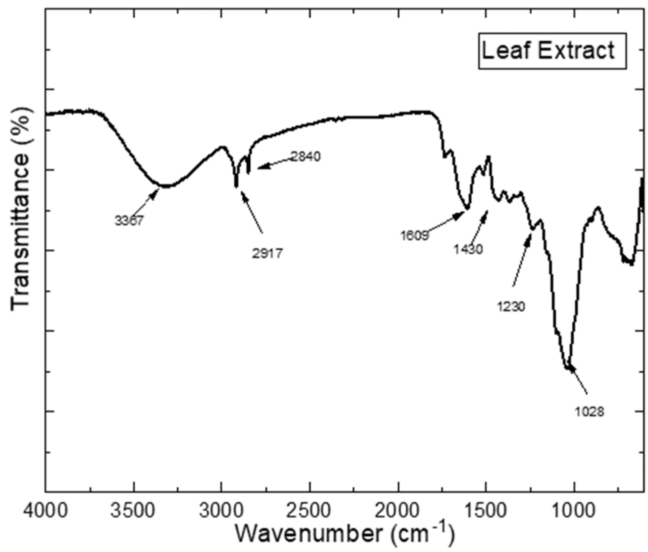

Figure 3. FTIR spectrum of date palm leaf extract.

A distinctive C═C stretching was noted at 1609 cm^{-1}, which can be associated with the aromatics as well as other carbonyl C═O stretching of polyphenols and flavonoids. Other distinctive peaks associated with the stretching of C−C and bending vibration of C−H in aromatic rings at almost 1430 cm^{-1}, together with the C−O group of polyols, like hydroxyflavonoids, were noted at almost 1230 cm^{-1}.[55] Similar results of the FTIR analysis were noted in a study carried out by peaks for Khalil et al.[56] These results obtained has confirmed the successful characterization of the palm leaf extract.

3.2. GQD Characterization. In the subsequent section, the results of the structural, morphological, and optical characterization of GQD-1 and GQD-2, synthesized from the date palm tree leaves, have been discussed. Furthermore, the product yields of the two types of prepared GQDs were also determined.

3.2.1. Analysis of Optical Properties. The optical properties of the developed GQD-1 and GQD-2 were investigated by performing the UV−vis absorption analysis. Generally, the absorption spectrum of GQDs exists in the ultraviolet region and the tail extending toward the visible region. The UV−vis spectra of GQD-1 and GQD-2 shown in Figure 4a,b show a significant absorption at almost 300 nm, which could be associated with the $n-\pi^*$ and $\pi-\pi^*$ transitions happening

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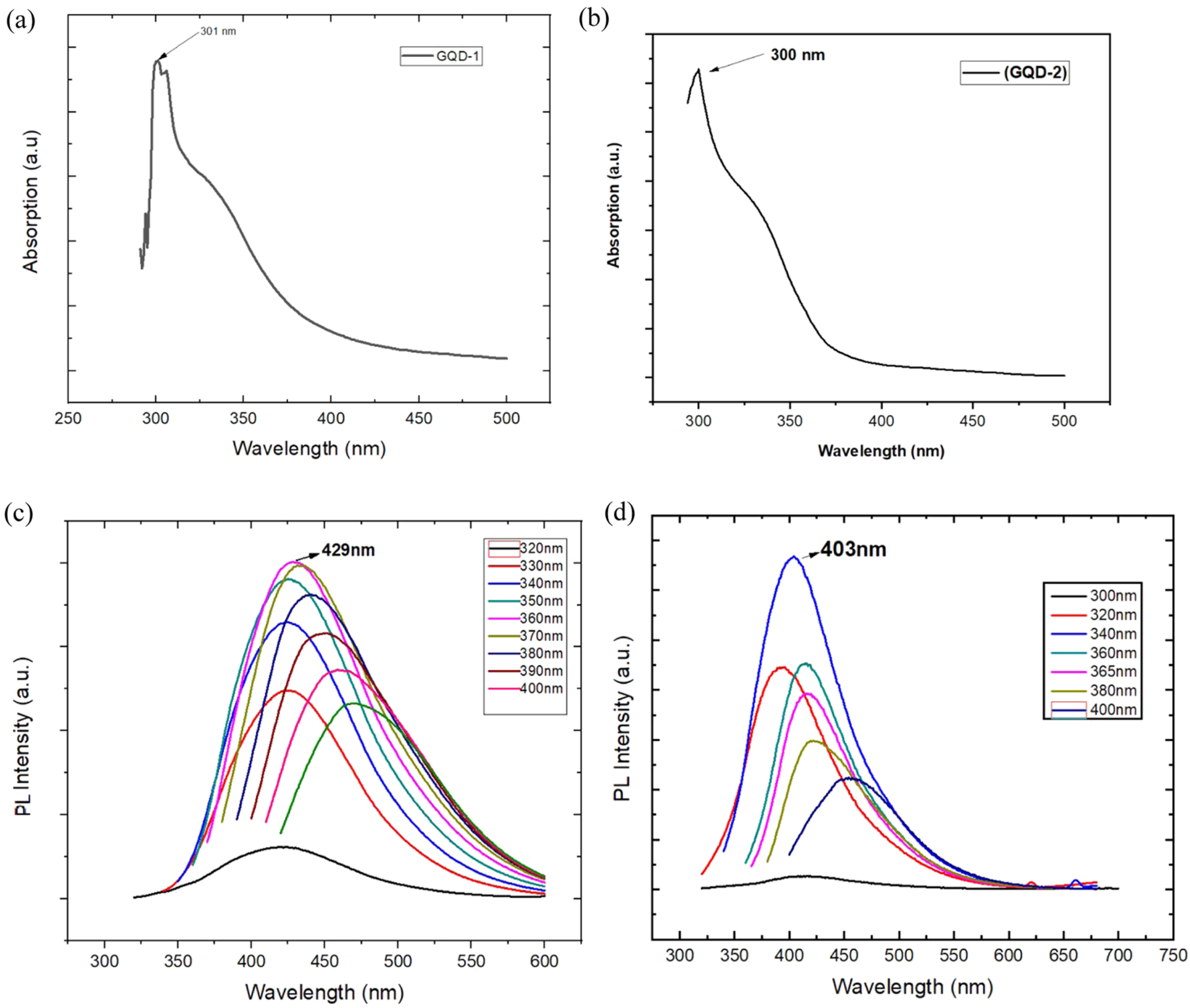

Figure 4. (a) UV−vis spectrum of GQD-1 from date palm leaves prepared as per method 1. (b) UV−vis spectrum of GQD-2 from date palm leaves prepared as per method 2. (c) PL spectrum of GQD-1 from date palm leaves prepared as per method 1. (d) PL spectrum of GQD-2 from date palm leaves prepared as per method 2.

from C═O groups and aromatic C═C bonds (sp^2 domain), respectively.[55] These results indicated that the UV absorbance in these GQDs is related to the surface oxygenated (C═O) states formed during the reaction.[56]

Figure 4c presents the PL spectrum of GQD-1 from date palm leaves prepared as per method 1, and Figure 4d presents the PL spectrum of GQD-2 from date palm leaves prepared as per method 2 in the current study. An analysis of the PL spectra of GQD-1 developed, at different excitation wavelengths from 320 to 400 nm, demonstrated an increase in the intensity of the emission till 360 nm and consequently decreased. The increase in the excitation wavelength led to the corresponding decrease in the PL emission intensity. As the excitation wavelength increases from 320 to 400 nm, the PL peaks shift to greater wavelengths, suggesting a red shift (430 to 480 nm).[57] At a wavelength of 360 nm, the excitation-dependent PL of GQD-1 was noted. The greatest photoluminescence intensity of GQD-1 was 429 nm, possessing a vibrational relaxation or dissipation of the wavelength at 173 nm. Similarly, an examination of photoluminescence spectra of GQD-2 developed, at various excitation wavelengths from 300 to 400 nm, demonstrated an increase in the intensity of the emission till 340 nm and consequently reduced. The greatest photoluminescence intensity of GQD-2 was 403 nm, with a vibrational relaxation or dissipation of the wavelength at 173 nm. The graphene quantum dot PL results obtained were consistent with the results obtained from several earlier findings.[58] The presence of hydroxyl as well as other functional groups with oxygen, the presence of conjugated aromatic hydrocarbons, the release of inhibited zigzag edges with a carbine-like triple ground state, and the emission that is trapped on the surfaces are noted as the main reasons for the GQDs' fluorescence emission mechanism.[59−61] The photoluminescence characteristic of graphene quantum dots at the excited state may be because of the optical selection of graphene quantum dots at various sizes as well as defects of GQDs on the surface level.[62,63] The major reason for the fluorescence in the excited stage is the carbon backbone of sp^2. The sp^2-conjugated domain of graphene quantum dots is

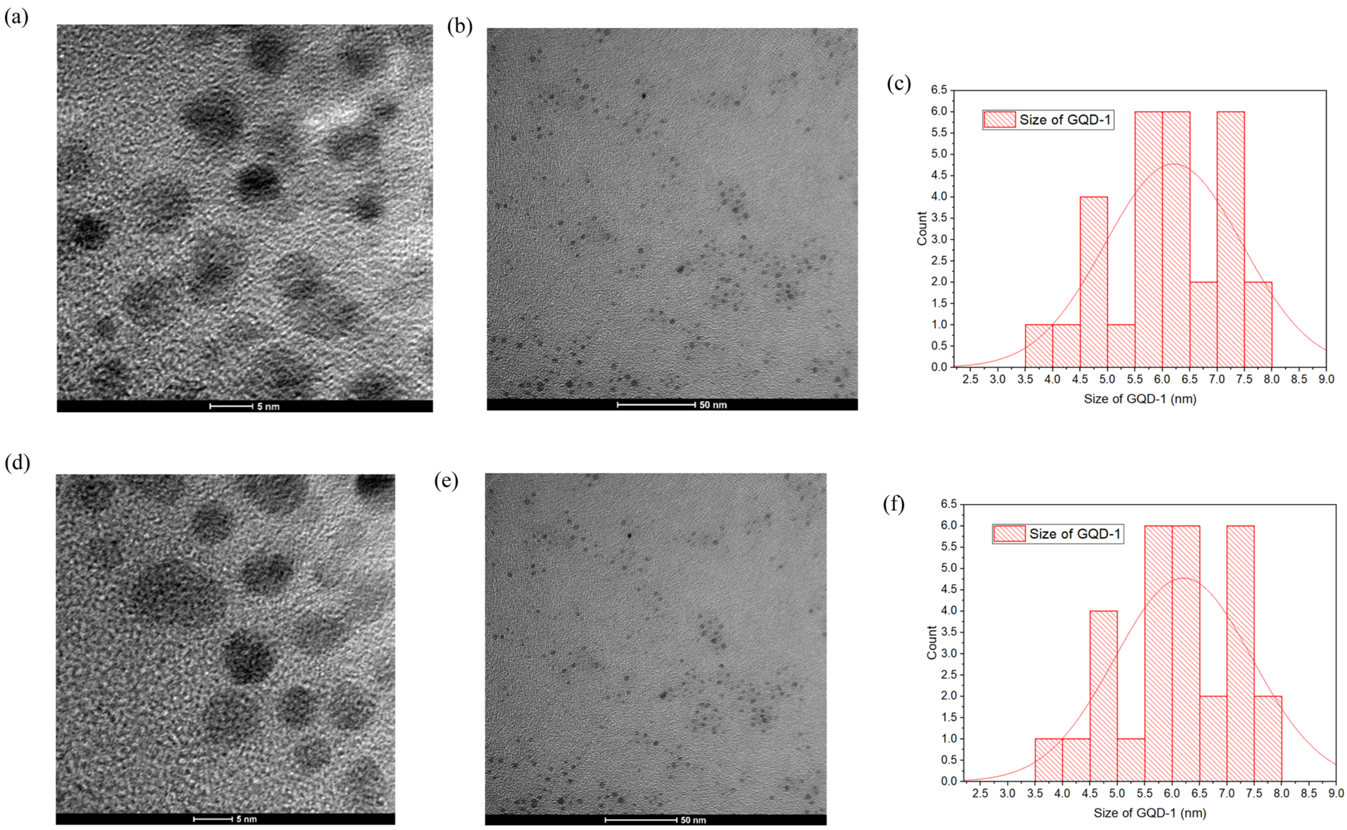

Figure 5. (a) TEM image (5 nm scale bar) of GQDs from date palm leaves prepared as per method 1. (b) TEM image (50 nm scale bar) of GQD-1 from date palm leaves prepared as per method 1. (c) TEM image particle size distribution of GQD-1 from date palm leaves prepared as per method 1. (d) TEM image (5 nm scale bar) of GQDs from date palm leaves prepared as per method 2. (e) TEM image (50 nm scale bar) of GQD-2 from date palm leaves prepared as per method 2. (f) TEM image particle size distribution of GQD-2 from date palm leaves prepared as per method 2.

sufficient to have a restricted energy gap in the band because of the effect of quantum confinement.[64]

3.2.2. Analysis of Morphological Properties. Figure 5a is the TEM image of GQDs from date palm leaves prepared as per method 1 at a 5 nm scale bar, and Figure 5b is the TEM image of GQDs from date palm leaves prepared as per method 1 at a 50 nm scale bar in the current study. The structure of GQD-1 from the analysis of TEM results proved that GQD-1 had sizes ranging from 3.5 to 8 nm (Figure 5c). Similarly, Figure 5d is the TEM image of GQDs from date palm leaves prepared as per method 2 at a 5 nm scale bar, and Figure 5e is the TEM image of GQDs from date palm leaves prepared as per method 2 at a 50 nm scale bar in the current study. The structure of GQD-2 from the analysis of TEM results established that GQD-2 had sizes ranging from 3.5 to 7 nm (Figure 5f). This is similar to the results obtained from the research work performed by Kumawat and his team members.[45] The formation of nanostructured GQD-1 and GQD-2 may be because of the carbonization of the solution during the heat treatment within the autoclave. The material's carbonization degree will help in regulating the size of GQD-1 and GQD-2 developed. Moreover, the GQDs prepared as per the current study were noted to be monodispersed spherical particles.

3.2.3. Compositional Analysis. From the FTIR spectra, the chemical bonding states of GQD-1 and GQD-2 were examined. Figure 6a shows the FTIR spectrum of GQD-1 from date palm leaves prepared as per method 1, and Figure 6b shows the FTIR spectrum of GQD-2 from date palm leaves prepared as per method 2 in the current study. GQD-1 showed stretching vibrations of the carbonyl group −C═O at 1645 cm^{-1}, C═C stretching vibrations at 1567 cm^{-1}, the hydroxyl group −OH at 3286 cm^{-1}, C−O stretching vibrations at 1420 cm^{-1}, and $-CH_2$ stretching at 2953 cm^{-1}. GQD-2 demonstrated stretching vibrations of the carbonyl group −C═O at 1751 cm^{-1}, C═C stretching vibrations at 1527 cm^{-1}, the hydroxyl group −OH at 3392 cm^{-1}, C−O stretching vibrations at 1399 cm^{-1}, and $-CH_2$ stretching at 2930 cm^{-1}. Thus, GQD-1 and GQD-2 prepared as per the current study confirmed that the carbonization reaction happened during the hydrothermal reaction. All of the findings in the FTIR analysis of the GQDs matched well with the results that were reported in several previous studies.[65−68]

Raman spectroscopy results of GQD-1 and GQD-2 are shown in Figure 7a,b, respectively. The results confirmed the presence of two different bands known as D- and G-bands. For GQD-1, the D-band was noted at 1381 cm^{-1} and this band was associated with the crystalline quality of the compound as well as the vibrational characteristics of carbon atoms with dangling bonds. Nevertheless, the G-band noted at 1590 cm^{-1} was related to the crystalline nature of the compound and E_{2g} vibration on the photon mode of sp^2 hybridization of the carbon atom in a two-dimensional hexagonal lattice of the graphitic framework (D, G).[68,69] Similarly, for GQD-2, the D-band is at 1364 cm^{-1} and the G-band at 1575 cm^{-1}. The intensity ratio of the disordered D-band and the amorphous G-

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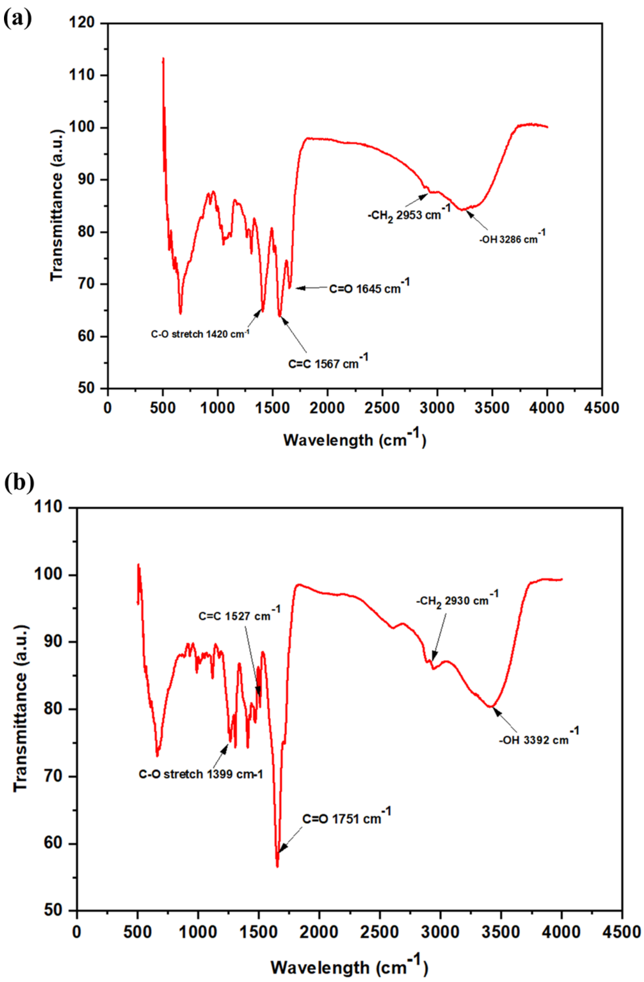

Figure 6. (a) FTIR spectrum of GQD-1 from date palm leaves prepared as per method 1. (b) FTIR spectrum of GQD-2 from date palm leaves prepared as per method 2.

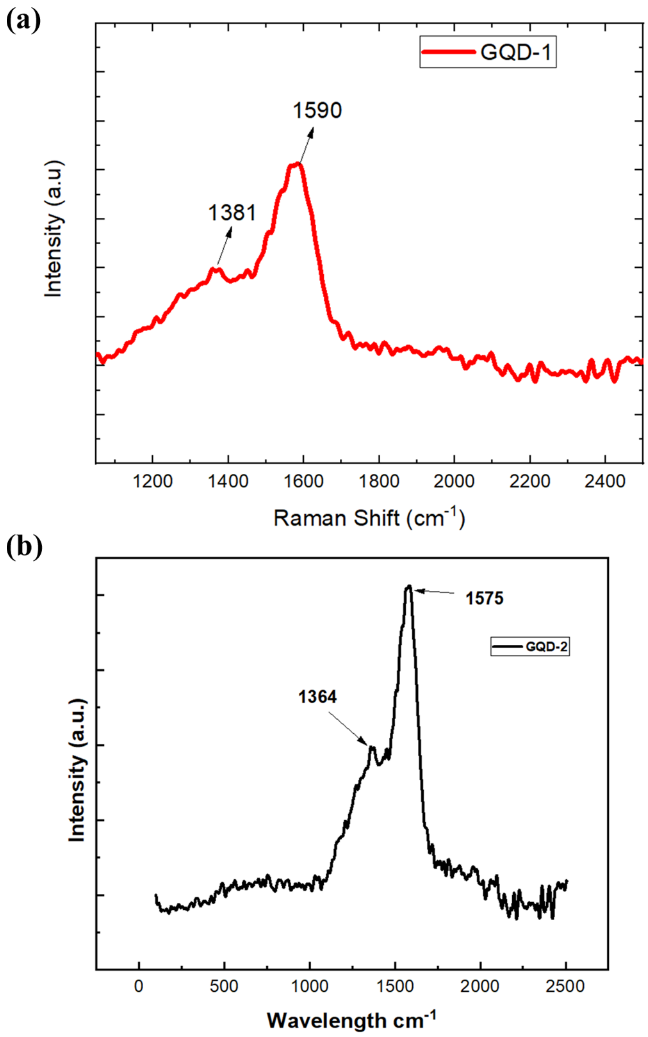

Figure 7. (a) Raman spectrum of GQD-1 from date palm leaves prepared as per method 1. (b) Raman spectrum of GQD-2 from date palm leaves prepared as per method 2.

band (D/G) is a conventional methodology for evaluating the homogeneity (degree of graphitization or disorder) of a GQD sample. A high D/G ratio is noted for an amorphous quantum dot specimen. A lower D/G ratio indicates a higher degree of graphitization in the GQD sample. In the current work, the D/G ratios of GQD-1 and GQD-2 were noted to be 0.523 and 0.866, respectively, and this confirmed that the developed GQDs demonstrated a nanocrystalline graphite structure, which is virtually the same as the results formerly published by other groups.[70,71]

Figure 8a presents the ^{1}H NMR spectra of GQD-1 in a D_2O solution, whereas Figure 8b demonstrates the ^{1}H NMR spectra of GQD-2 in a D_2O solution. In the ^{1}H NMR of both samples, it can be noted that the water peak is very high at 3.74 compared to other peaks' heights because both samples have moisture content, which is tried to be removed by heating. However, it was found that at 100 °C the solution started sticking on the wall of the beaker and began to deconstruct. In both the samples, the ^{1}H NMR spectrum regions were found at 1−3 ppm (for sp^3 C−H protons), 3−6 ppm (for the protons attached with hydroxyl, ether, and carbonyl groups), 6−8 ppm (for the aromatic or sp^2 protons), and 8−10 ppm (for the aldehydic protons). These results matched the spectrum obtained in a study carried out by Song et al.[72]

3.3. Product Yield of GQDs Developed.

The yields for GQD-1 and GQD-2, developed as per method 1 and method 2, respectively, were noted to be 52 and 49.2%, respectively. Hence, considering the higher yield of method 1, it was considered to be more beneficial out of the two methods in this study.

From the characterization data, it was observed that the properties of the GQDs obtained using the two methods were almost similar. However, the GQD-2 preparation involves the usage of ethanol, thereby increasing its production expenses. Therefore, it was concluded that method 1 was preferred over method 2, since it was entirely environmentally friendly with the usage of just DI water and had good yield and less production expenses. These GQDs developed, as per method 1 and method 2, are noted to have immense possibilities of application in nanomedicine, bioimaging, biosensing, drug delivery, membranes in water filtration, catalysis, carbon fixation, fuel cells, and gas sensors.

4. CONCLUSIONS

As there is mass production of date palm tree biowastes every year, the possible usage of palm tree residues for nanomaterial preparation is of great significance. The standard preparation

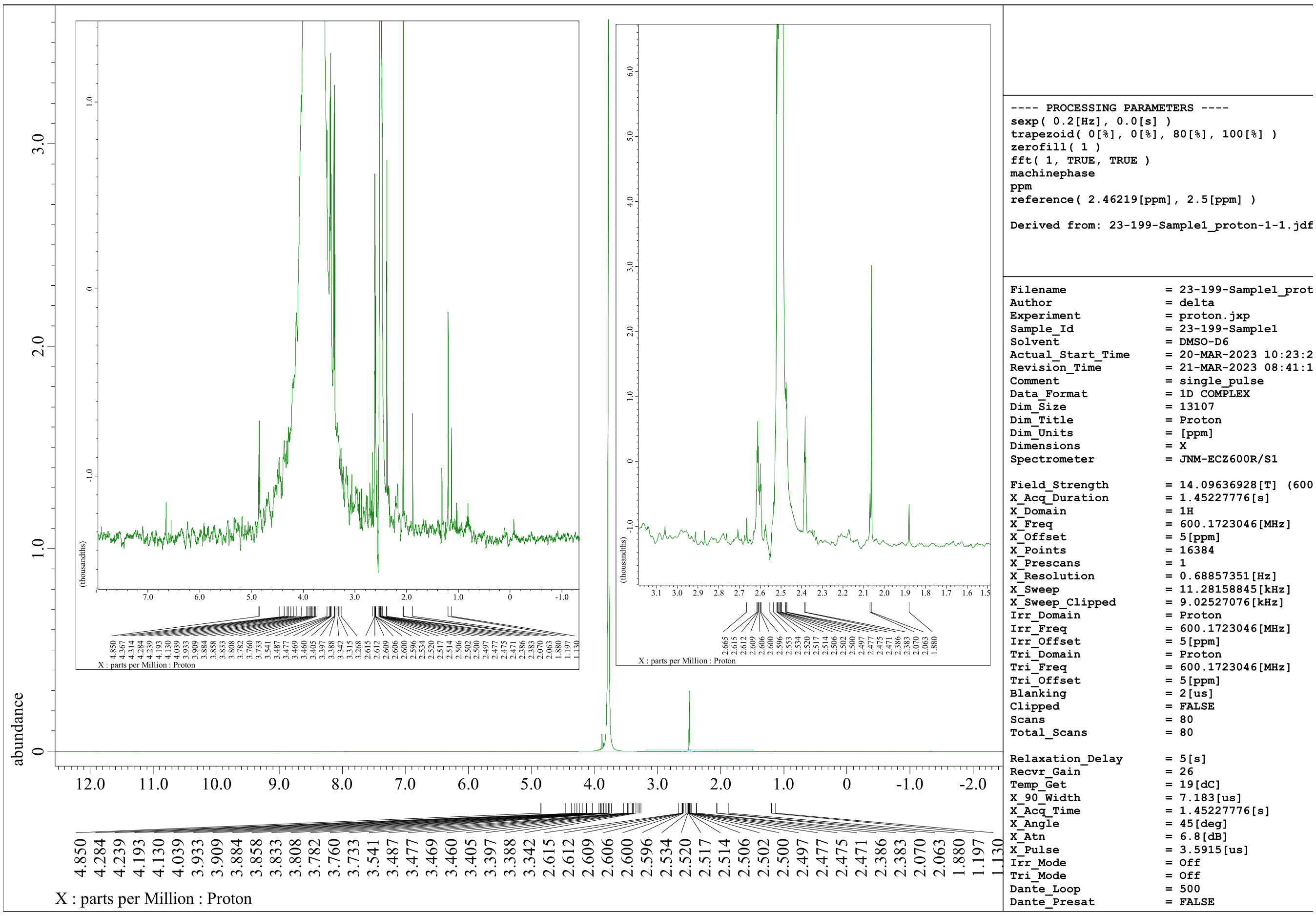

Figure 8. (a). ^{1}H NMR spectra of GQD-1 in a D_2O solution., (b) ^{1}H NMR spectra of GQD-2 in a D_2O solution.

of GQDs requires high-quality carbon precursors, toxic organic solvents, high temperatures, concentrated acid/alkali treatments, and complex purification methods. In the present research work, GQDs are developed from the date palm tree biowaste using two methods. The first method employs the utilization of just distilled water without using any chemicals during its synthesis. The second method involves the use of distilled water and absolute ethanol for the GQD synthesis, and the ethanol used during the GQD-2 synthesis is removed eventually during the process, thereby making it as sustainable process. The TEM results confirmed the successful formation of GQDs with sizes in the range of 3.5−8 nm for GQD-1, whereas 3.5−7 nm for GQD-2. The UV−vis absorption spectrum demonstrated a stronger background absorption at approx. 304 and 300 nm for GQD-1 and GQD-2, respectively, because of the $\pi-\pi^*$ transition of the aromatic sp^2 domains. The Raman analysis confirmed that GQDs developed had a nanocrystalline graphitic framework. Thus, this work helps to obtain GQDs in an economical, eco-friendly, and biocompatible manner and can help in large-scale production and in recycling date palm tree waste products from Middle East countries into value-added products. The yields obtained for GQD-1 and GQD-2 were noted to be 52 and 49.2%, respectively. From the analysis of characterization data, it was observed that the properties of the GQDs obtained using the two methods were almost similar. However, the GQD-2 preparation involves the usage of ethanol, thereby increasing its production expenses. Therefore, it was concluded that method 1 was preferred over method 2 due to the fact that it was entirely environmentally friendly with the usage of just DI water and had good yield and less production expenses.

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Notes

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