Biowaste valorization of palm tree *Phoenix dactylifera* L. for nanocellulose production

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Research Article

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Abstract

The desire to reduce reliance on oil resources arises from the concerns about carbon footprint and nonrenewability. Conversely, the global presence of over 100 million palm trees poses a significant challenge due to the substantial amount of biowaste generated annually. Additionally, the use of nanocellulose as a cost-effective material is steadily gaining recognition for its growing adaptability over time. This research focused on the utilization of Iraqi date palm Phoenix dactylifera leaves waste, with low concentration acid-alkali treatment was used to produce nanocellulose. This part yields were 20 gm of nanocellulose from 100 gram of leaves before acid hydrolysis treatment, The chemical components of biosynthesized nanocellulose were 47.90, 26.78 and 24.67 for α-cellulose, hemicellulose and lignin respectively. Extraction of nanocellulose from raw date palm leaves was confirmed by scanning electron microscopy (SEM), energy dispersive x ray spectroscopy (EDX) and atomic force microscope (AFM). SEM results revealed rod like structured nanocellulose as well combined long-fine fibrous structures rather than compacted bundle with sizes ranging between 31 and 74 nm. With EDX, all spectra exhibit the peaks of carbon and oxygen as the main elements with 63.8% and 10.44% respectively in their compositions, which relate with the typical composition of cellulose. the 3D image of nanocellulose with a tapping mode highly uniform distribution of particles with many peaks. The statistical roughness analysis shows that the obtained roughness average is 7.20 nm with the root-mean-square (RMS) roughness value of 21.56 nm which corresponded relatively with the micrographs of SEM. The results of this study demonstrate the promise of using date palm waste as raw material to produce nanocellulose as green nanocomposite from biodegradable nanomaterial for water purification and sustained drug delivery for biomedical applications.

1. Introduction

The increased focus on the utilization of natural biopolymer fibers, as opposed to synthetic fibers, has prompted researchers to investigate various sources of biodegradable natural fibers. Among the available options, cellulose stands out as the most abundant renewable biopolymer fiber. Cellulose is primarily composed of D-glucose and consists of a linear and unbranched homopolysaccharide structure. It is worth noting that this biopolymer exhibits remarkable thermal and mechanical stabilities, while also demonstrating minimal to no toxicity towards the environment [1].

With an estimated annual production of approximately $7.5 \times 10^{10}$ tons, cellulose can be considered as potentially the most abundant natural biopolymer found on our planet. Cellulose, a high-molecular-weight homopolymer, is comprised of repeating units of β-d-glucopyranosyl that are connected through (1→4) glycoside linkages, and can be extracted from various biomasses [2]. Cellulose is composed of both crystalline and amorphous regions. By employing acid hydrolysis treatment [3], the amorphous area of cellulose can be removed, resulting in the formation of crystalline particles known as nanocellulose (NC) or cellulose nanocrystals (CNCs) that exhibit noteworthy attributes such as cost-effectiveness, non-toxicity, excellent thermal stability, optical transparency, and biodegradability [4].
Due to its exceptional thermal and mechanical properties, NC is extensively employed as a reinforcing agent in polymer composites. The incorporation of NC significantly enhances the physicochemical, thermal, and insulating characteristics of various biodegradable polymers, thereby enabling their suitability for a wide range of applications [5]. Iraq, known as the originating hub of the date palm, holds historical significance as the site of domestication for this particular crop. Additionally, Iraq held the distinction of being the global leader in date production for a significant span of time, both historical records and genetic testing provide evidence that Iraq serves as the birthplace of the date palm, scientifically known as *Phoenix dactylifera*. This country, since 4000 B.C., has witnessed the domestication and cultivation of this tree. Moreover, it holds a significant historical background and the consumption of palm dates has always played a crucial role in its culture. These dates not only constitute a major agricultural product but also symbolize the identity of the nation, as they are depicted on our currency. The inhabitants of Iraq have extensively utilized this tree for sustenance, medicinal purposes, the creation of furniture, and an assortment of household utensils [6].

Each year, trees can produce about 200,000 tons of lignocellulosic waste after planting or fruit harvesting (branches, stalks and trunks). Meanwhile, these agro-wastes can be used in the production of environmentally friendly materials with low costs for many applications, such as in textile, baggage, sports item, and automotive parts [7–9]. In this regard, the objective of this study is to acquire nanocrystalline cellulose from a unique variety of fibers sourced from the waste of Iraqi date palm leaves, with the intention of employing it as a strengthening agent for biocomposites utilized for industrial applications. Additionally, it has the potential to serve as a primary material for the isolation of nanocellulose to facilitate the development of Bio-nanocomposite materials in the future.

2. Material and Experimental

2.1 Materials and Chemicals

The leaves of Iraqi date palm *Phoenix dactylifera* L. were collected from the north of Baghdad’s Orchard. Sodium chlorite (80%), Sodium hydroxide (97%), acetic acid glacial (99.9%) and sulphuric acid (95 to 97%) all the materials were employed in their original form as acquired from the supplier.

2.2 Nanocrystalline Cellulose Extraction Process

2.2.1 Cleansing Technique

Upon washing and cutting, the date palm fibers were mechanically crushed (see Fig. 1a) and subsequently submerged in water at a temperature of 100°C, while being stirred for 1 hour, in order to eliminate any solutes present. Subsequently, these fibers were dried under vacuum conditions at a temperature of 50°C for a period of 15 hours.

2.2.2 Alkaline Treatment
In order to obtain pure cellulose, the date palm fibers were subjected to a 4 weight% sodium hydroxide (NaOH) solution for 2 hours at a temperature of 80°C. The resultant mixture was then filtrated and washed multiple times with distilled water, following which it was dried under vacuum conditions at a temperature of 50°C for a duration of 24 hours.

This treatment was repeated twice

### 2.2.3 Bleaching Treatment

Post alkaline treatment, a 1.7 wt.% solution of sodium chlorite (NaClO2) was prepared, and acetic acid was added until the solution reached a pH of 4. Subsequently, the palm fibers were treated with this solution at a temperature of 80°C for a duration of 2 hours. The mixture was then filtrated using distilled water to procure white-colored fibers, which were subsequently dried in a vacuum oven at a temperature of 50°C for a duration of 24 hours. The bleaching treatment was achieved twofold to purify the cellulose component, Fig. 1c.

### 2.2.4 Acid Hydrolysis Treatment

Subsequently, the pulp fiber was treated via 64 wt. % of sulphuric acid (H2SO4) solution at 45°C for 30 min under steady stirring. The resulted mixture was filtered and washed thoroughly with distilled water to ensure removal of acid, then it was dehydrated at 50°C in a vacuum oven for 24 h. [10]

### 2.3 Yield Determination

The NC yield was calculated using Eq. (1), as given:

\[
\text{Yield} \, (%) = \left( \frac{M_1}{M_2} \right) \times 100\% \tag{1}
\]

in which \(M_1\) is the weight of oven-dried NC, and \(M_2\) is the weight of raw date palm.

### 2.4 The chemical compositions of nanocellulose

The chemical compositions of nanocellulose were determined such as α - cellulose, hemicellulose, lignin, according to Poddar et al. [11].

### 2.5 Microscopic analysis

#### 2.5.1 Light microscope

After acid hydrolysis treatment the palm fibers with the biosynthesized nanofibrils was examined under a light microscope at 40X magnification after staining with eosin dye to confirm the decomposition of the fibers for nanocellulose production, which will be confirmed using the scanning electron microscope

#### 2.5.2 SEM analysis

The morphological structure of chemical treated biomass was investigated using Scanning Electron Microscope SEM (Hitachi) equipped Energy Dispersive X-ray (EDX) was also used to examine the
elements composition that identified samples at 1000× magnification. Dry powder sample was placed on carbon tapes and then sputtered with thin gold layer under argon atmosphere.

### 2.5.3 Atomic force microscopy

Atomic Force Microscopy (AFM) examination was used by dropping aqueous cellulosic nanoparticles steadily on a glass slide then it was dried by air before investigation. Then images were captured by applying tapping mode on the NC samples with a scan rate of 4.80–6.00 μm/s at ambient condition.

### 3. Results

The Iraqi date palm biowaste yielded 20 gm of cellulose from 100 gram of oven-dried leaves before acid hydrolysis treatment, the yield percentage exhibited by this work is found comparable to study by [12] showing the yield percentage of fronds 2.9 gm, The present of the chemical components of biosynthesized nanocellulose were shown in Table 1. the α-cellulose content of date palm raw sample with 47.9% while hemicellulose represents 26.78% from the total component, the lignin was represent 24.67%, this results was possibly similar with other lignocellulosic materials that candidate this product to use as a natural source of biodegradable cellulose.

<table>
<thead>
<tr>
<th>Product</th>
<th>α- cellulose %</th>
<th>Hemicellulose%</th>
<th>Lignin%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocellulose</td>
<td>47.90</td>
<td>26.78</td>
<td>24.67</td>
</tr>
</tbody>
</table>

Cellulose is the most abundant polysaccharide in our planet because it is the main building compound for utmost plants. It is a linear homopolymer made up of glucan chains with repeating (1–4)-D-glucopyranose units connected by O-glycosidic bonds [12].

The size and morphology of nanocellulose extracted from the palm waste were demonstrated by the light compound and SEM microscopic analysis as illustrated in Figs. 1 and 2.

The Fig. 1 was indicates the destruction of the plant cells especially the fibers of the palm leaves after acidic treatment and the production of nanocellulose, as a comparison with palm leaves before the acidic treatment. It is observed that palm leaf fibers were break and appear as irregular bundle, which indicates the possibility of producing cellulose at the nano scale that confirmed by SEM analysis.

As that SEM investigation is achieved on dry powder sample. The fronds residues nanocellulose show the swelling of cellulose was observed followed by isolation of rod like structured cellulosic nanoparticles appeared as well combined long-fine fibrous structures rather than compacted bundle with sizes ranging between 31 and 74 nm, additionally to the high intensity electron beam during SEM study splitting, With the acidic treatment, the nanoparticles had further broken into shorter crystallites as showed by Fig. 2 These results are much better compared to some literature by [13]
The small particle size of biosynthesized nanocellulose was a promising starting material for industrial application. The width of nanocellulose for current work was better in comparison to widths yielded by [14] with 42–82 nm spherical particles.

The EDX analysis of palm date fronds were shown in Fig. 3 table 2, All EDX spectra exhibit the peaks of carbon and oxygen as the main elements with 63.8% and 10.44% respectively in their compositions, which relate with the typical composition of cellulose [15], This confirmed that the cellulose compartments for those nanocellulose were different as a result of the different hydrolysis treatment [16] as well as sulfur element with 22.25% that may deposit as result of the acidic hydrolysis treatment which indicating the applicable extraction of nanocellulose from palm date fronds, for nitrogen, the weight was 3.5% may appeared as result for fertilizers of the date palm in Iraq as a result of the harsh conditions that the country went through as wars, high salinity and pest invasion.

Table (2) illustrated the weight percent for the elemental composition of the cellulosic nanoparticles extracted from palm date fronds after acid hydrolysis treatment

<table>
<thead>
<tr>
<th>element</th>
<th>Weight%</th>
<th>Pk/Bg</th>
<th>LConf</th>
<th>HConf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N)</td>
<td>3.50</td>
<td>45.74</td>
<td>3.12</td>
<td>3.88</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>63.80</td>
<td>201.20</td>
<td>62.47</td>
<td>65.14</td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>10.44</td>
<td>49.60</td>
<td>9.89</td>
<td>10.99</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>22.25</td>
<td>59.20</td>
<td>21.73</td>
<td>22.77</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
<td></td>
<td></td>
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</tbody>
</table>

The topographic image of AFM Fig. 4 shows the 3D image of nanocellulose with a tapping mode highly uniform distribution of particles with many peaks. The statistical roughness analysis shows that the obtained roughness average is 7.20 nm with the root-mean-square (RMS) roughness value of 21.56 nm which corresponded relatively with the micrographs of SEM. The AFM results show that the roughness and well-dispersed surface of nanocellulose, previous studies by [17] have reported relatively a similar finding.

4. Conclusion

The findings of the present study demonstrate the feasibility of utilizing acid hydrolysis to extract nanocellulose (NC) from date palm biowaste. The resulting nanoparticles exhibited a rod-like morphology, and their desirable nano-sized ranging between 31 and 74 nm with high content of α-cellulose was advantageous for nanocomposite processing. Consequently, the isolation of NC from date palm leaves offers a promising alternative for the development of nanocellulose products in the future.

Declarations
no conflict of interest exists for all participating authors

References


**Figures**
Figure 1

illustrated the raw date palm leaves after acidic hydrolysis under light microscope with 40 X magnification.
Figure 2

SEM images for the obtained nanocellulose with low (A) and high (B) magnification showing the shape and size of the obtained particles after the acidic hydrolysis process.

Figure 3
The EDX patterns of cellulosic nanoparticle biosynthesized from palm date fronds.

Figure 4

(A) and (B) 3D image of AFM for biosynthesized nanocellulose and (C) size distribution from histogram image of nanocellulose