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Research Article
Isolation Cellulose Nanofibers from Date-Palm Tree Leaflets (*Phoenix dactylifera* L.) by Ball-Milling Technique

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Abstract

Background and Objectives: Unlike chemical methods, the mechanical ball milling technique has been relied upon because of its environmentally friendly advantages and chemical saving. This study aims to use a simple approach to convert agricultural waste into value-added materials to be utilized in water purification and treatment uses. **Materials and Methods:** In this work, we extracted and characterized cellulose nanofibers from palm trees (*Phoenix dactylifera* L.), a cellulose-rich by-product and abundant in the local environment. First, cellulose fibres were extracted from leaflets of date-palm through alkaline treatment using sodium hydroxide. Then, the extracted cellulose was directed to bleaching and soaking. The soaked-bleached cellulosic material was ball milled, via Micro Mill PULVERISETTE 7, at different grinding rates (30, 60, 90 and 120 min, at 400 rpm) without chemicals. **Results:** The alkaline treatment helped to remove the defibrillation due to the weakening of the hydrogen bonds in the cellulose and provided an additional process, which increases the consumption of environmental resources. TGA thermogram curve shows that lignin and hemicelluloses were completely removed under the effect of the alkali treatment of the bio-mass and no thermal change at higher milling time. The results of the XRD showed that the higher the milling rate, the higher degree of crystallinity is. The morphology of the CNFs (SEM) demonstrates fibrous network nanostructures with a diameter of 20-30 nm at a higher milling rate. **Conclusion:** Ball milling was found as an effective process to transfer the extracted cellulose into nanofibers (CNFs). The alkaline treatment helped to remove the defibrillation due to the weakening of the hydrogen bonds in the cellulose and provided an additional process, which increases the consumption of environmental resources.

Key words: Date-palm tree, cellulose extraction, cellulose nanofibers, ball-milling technique, nanocellulose, agro-waste, alkaline hydrolysis

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Nowadays, nano-cellulose has become a substance of great importance and within the last ten to fifteen years, many researchers oriented their interest in converting cellulose into renewable value-added materials[1-3]. The countless functional groups of cellulose facilitate the formation of an active surface by chemical treatment making it a material of various applications.

Therefore, nano cellulose materials have gained much attention and research interest due to their potential applications. They widely can be used in many fields such as nanocomposite materials[4], food additives[5], filling materials in polymer industry[6] and pharmaceuticals as drug delivery[7-8]. They are considered eco-friendly materials with many advantages, such as high surface area, renewability, specific high strength and modulus and good optical properties.

Cellulose is a natural organic compound found in plants fibres. It is considered one of the most abundant the earth. About 33% of plants' constituents are cellulosic components. Cellulose is a linear polymer of as many as 10,000 D-glucose units (Fig. 1). It is used in the industry for making paper, cardboard, cellophane and rayon[9].

Date-palm tree, *(Phoenix Dactylifera* L.), is one of the plants that are rich in cellulosic fibers[10]. The numbers of cultivated date-palm trees in Arab countries exceed 85 million trees[11]. Specifically, in the Kingdom of Saudi Arabia, the latest statistics reported that the number of palm trees exceeds 28 million in 160 thousand hectares, representing about 55% of the total domestic production of fruit produced by almost 120 thousand farms. In contrast, the local Agriculture sector produces about 1.7 billion tons every year of date-palm tree wastes and agricultural products[12]. Our goal is to convert these by-products into valuable materials that can be exploited into efficient potential utilizations. Due to the lack of studies related to cellulose nanofibers from a local date-palm tree, herein is a study of preparing cellulose nanofibers from date-palm tree waste (e.g., fronds leaflets) characterization the obtained nanomaterials.

Researchers classified nanocellulose materials in three main types: Cellulose nanofibers (CNF), which is also sometimes called nanofibrillated cellulose (NFC), Cellulose nanocrystals (CNC), which are also sometimes called nanocellulose whiskers and bacterial nanocellulose (BNC)[13]. The nanocellulose materials are biodegradable, renewable, recyclable, environmentally friendly and abundantly available nearly everywhere in the world. Uses of nanocellulose materials are in medicines, biocomposites, pharmaceuticals,

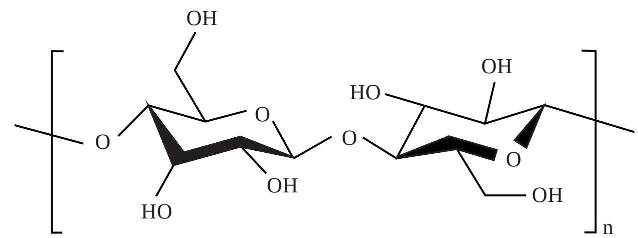

Fig. 1: Cellulose structure

batteries, biosensors, aircraft, paper coatings, tissue engineering and many other applications. Researchers are interested in CNF more than CNC. Cellulose nanofibers (CNFs) with crystalline and amorphous sections can be isolated from cellulose microfibers[14]. At the same time, some researchers prepare CNF by mechanical fibrillation, such as milling based on the source of cellulose and chemical pretreatments[15-19]. They are an eco-friendly approach to converting low-cost biomass into CNF. In some cases, pretreatments (enzymatic pretreatment, chemical pretreatment, or mechanical pretreatment) are carried out on CNF to reduce energy input, enhance CNF quality or achieve other purposes[20].

The ball milling technique is a cost-effective technology with vast potential. It is applicable for preparing cellulose nanofibers or nanocrystals. This technique is adequate because it can be combined with chemical treatments to obtain the wanted products with minimal effort[21]. Although ball milling technology has been exploited in process engineering, organic synthesis and the formation of nanocomposites, its potential to isolate and chemically modify cellulose nanoparticles has not been fully explored, as only a limited number of studies has been carried out. On the other hand, preparation CNFs by ball-milling was to be optimal when preparation is performed in wet conditions to feasible the fibrillation. In the literature, some studies reported preparing nanofibers by ball-milling. Phanthong *et al.*[22] produced nanocellulose by planetary ball milling from cellulose powder with ionic liquid at room temperature. It is a facile one-step method for extraction nanocellulose with great efficiency and high yield. Wang *et al.*[23] prepared nanocomposite from nanocellulose and ultrahigh molecular weight polyethylene using the ball milling method at 200 rpm for six hours. This result is suitable for utilizing this polymer in medicine. A recent study dealt with utilizing biomass as a source for obtaining cellulose nanofibers by ball milling. Radakisnin *et al.*[24] prepared cellulose nanofibers from Napier fibre *(Pennisetum purpureum)* using acid hydrolysis as an aid for fabrications to facilitate cellulose fibre size reduction. Another study showed that cellulose nanofibers CNF, with size below 500 nm, can be prepared by dry and wet ball milling from biomass wastes (e. g., jute fibre wastes)[25]. CNF also be obtained from bamboo fibre from mechanical treatment, enzyme activation, carboxymethylation and ultrasonic homogenization[26]. Teixeira *et al.*[27] used different types of cotton fibres using acid hydrolysis with 6.5M of sulfuric acid at 45°C to produce CNFs. They concluded that extraction yield, sulfonation efficiency and thermal stability varies according to the type of cotton fibers[27]. They found that extraction yield, surface charge and carboxymethylation reaction were enhanced through the existing preparation procedures. Based on these studies, it can be concluded that preparation and isolation processing play is a crucial part in cellulose nanofiber production. However, the production of Nano-cellulose fibre from palm date trees by using ball milling is not sufficiently reported. This work is an attempt to use the ball milling technique to transfer the cellulose extracted from palm date tree into Nano-fiber wither desired Nanofiber properties, based on green chemistry and simple processing.

MATERIALS AND METHODS

The study was carried out at the Department of Chemistry at Imam Muhammad ibn Saud University from October-June, 2019.

Materials: Leaflets of the date palm tree (LDPT) were collected from a local farm in Riyadh province, Saudi Arabia. Sodium hydroxide (NaOH), acetic acid (CH_3COOH) and sodium chlorite ($NaClO_2$) was highly graded laboratory chemicals where purchased from BDH chemicals.

Extraction of cellulose: After collecting raw materials, they were cut into small sizes (ca. 2-3 mm), washed with distilled water three times to remove dust and impurities and then well-dried in a sunny area for one day until the complete drying. After drying, they were ground and dried at ambient temperature using a stainless-steel grinder. About one-hundred grams of the raw materials (LDPT) were soaked in a considerable amount of water for 24 hrs. Then, they were filtered and placed into a round-bottle flask containing 200 mL 5% sodium hydroxide for hydrolysis purposes. The hydrolysis process using sodium hydroxide was performed at 90°C for 2 hrs under reflux. The matrix was filtered and washed with de-ionized water several times until neutral pH. Then, the residue was dried in an oven at 80°C for 4 hrs.

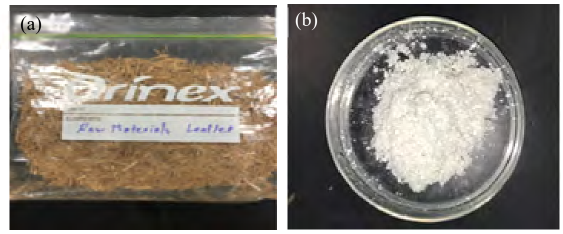

Fig. 2(a-b): Photos of (a) Raw materials and (b) Extracted cellulose

Bleaching process: The process was achieved using 1.7% sodium chlorite at a fixed pH value of 4.5 (using acetic acid as pH maintaining), the bleaching process was carried out under stirring at 75°C until clear white colour as a result of lignin leaching[19]. The matrix was filtered, washed with de-ionized water until neutral pH and dried in an electric oven at 80°C for 6 hrs and kept in the dark sealed containers for 24 hrs, (Fig. 2a-b).

Preparation of cellulose nanofibers by ball-milling: The ball mill used in this procedure was a planetary micro mill PULVERISETTE 7 (Fritsch, Idar-Oberstein, Germany) classic line with 45 mL tempered steel vials and 10 mm tempered steel grinding balls. The dry hydrolyzed LDPTs were soaked in distilled water with a solid to water ratio of 1:20 (w %) overnight at room temperature. Then, the slurry of four samples was put into the steel vials for milling at 30, 60, 90 and 120 min at 400 rpm. The samples were washed three times with cold de-ionized water by centrifugation at 10,000 rpm at 15 min. The supernatant was discarded and the suspension was collected and spread into glass plates. The obtained samples were dried in an oven at 60°C for two hours and then in the air for one day to prepare them for characterization.

Characterizations of the prepared nanofibers

Fourier Transform Infra-Red Spectrometry (FTIR): A Fourier transform infrared spectroscopy (PerkinElmer Spectrum Version 10.5.2) was used to record the FTIR curves in the transmission mode, between 4000 and 650 cm^{-1}, pathlength of 1 mm. The four samples were scanned (for each sample) with a resolution of 4 cm^{-1}.

X-ray diffraction (XRD) analysis: Characterization of the prepared CNFs in this study was performed with X-ray powder diffraction (XRD) measurements are performed by D8 brucker diffractometer with Cu-k radiation (λ = 1.54178) in the range 2θ = 10-70° at 0.02° step size . Samples were subjected to the radiation in the perpendicular direction.

Scanning electron microscopy (SEM): The SEM images of the obtained CNFs were recorded by JSM-IT 300 HR (JEOL, Japan) at 10 kV accelerating voltage. The samples were placed on a holder of metal and coated with gold.

Thermogravimetric analysis (TGA): The thermal stability of the prepared CNFs was studied by a PerkinElmer STA-6000 instrument. The TGA curves of samples were measured at a heating rate of 10°C per min in the range of 30°C to 1100°C under a continuous nitrogen flow of 20.0 mL/min.

RESULTS AND DISCUSSION

The obtained cellulose nanofibers need to be characterized via some important measurements such as FTIR, XRD, SEM and TGA. The FTIR spectra of extracted cellulose and the four ball-milled samples are shown in Fig. 3 and Fig. 4a-d, respectively. The spectra in Figure 4a-d clearly show the convergence between the four samples, pointing out that all have the same chemical composition and display a slight difference with IR of extracted cellulose (Fig. 3). The figure will show peaks around 900-1000 cm^{-1} (glycoside deformation and vibration) and it attributed to amorphous cellulose, the peak around 3600 cm^{-1} is characterized by the cellulose -OH vibration, this beak disappeared in all ball-milled samples indicating the progress of the process and homogeneity in hydrogen bonding patterns[28]. Bands at 2950-3030 cm^{-1} refer to CH stretching. Likewise, these bands may be attributed to the carbon-hydrogen symmetrical stretching of both cellulose and hemicellulose[24]. Multiple peaks around 1220, 1370 revealed the stretching vibration of cellulose and C-H bending, respectively and peaks around 1440 cm^{-1} are attributed to the C-O bending vibration of cellulose.

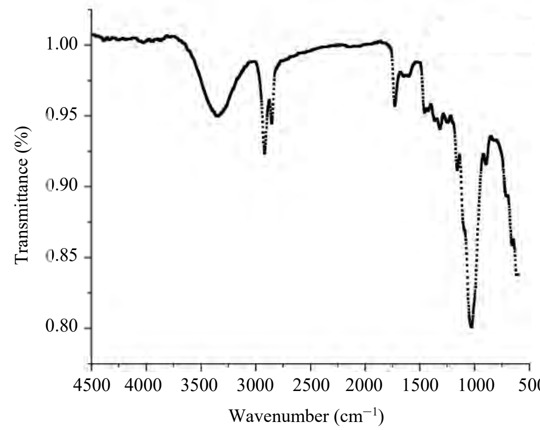

Fig. 3: FTIR spectrum of extracted cellulose after bleaching

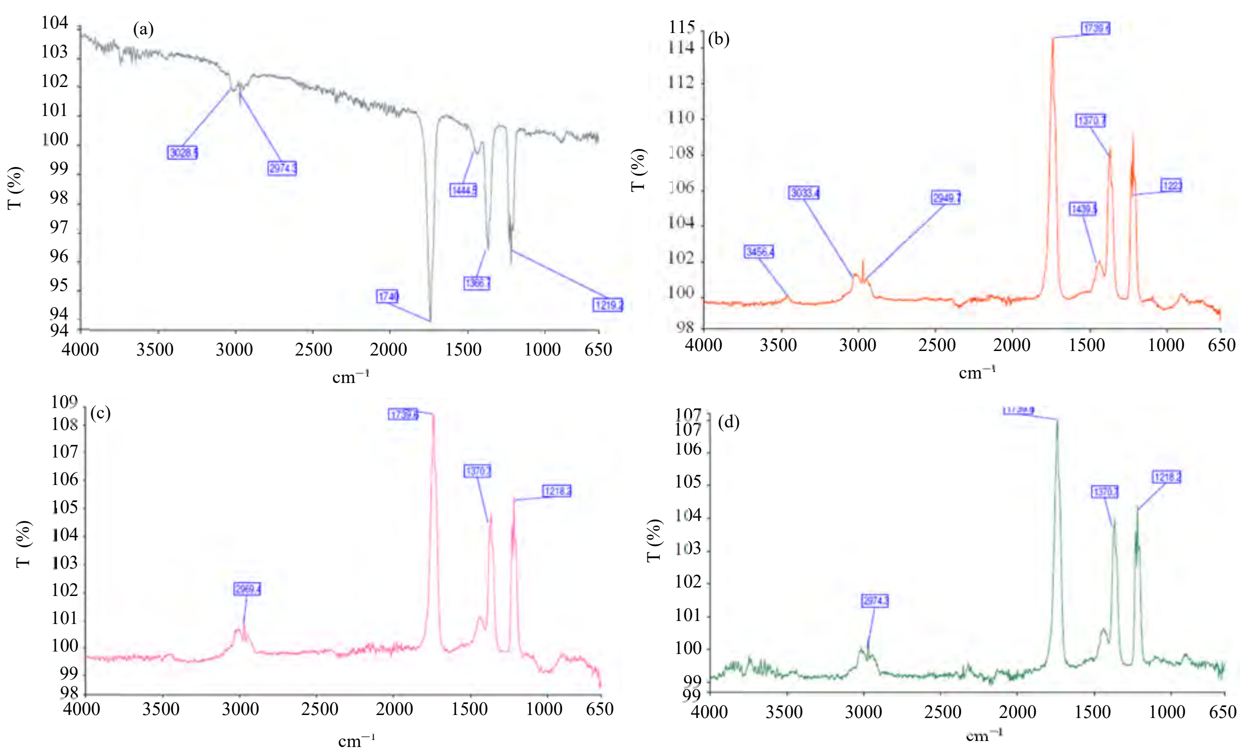

Fig. 4(a-d): FTIR spectrum of Ball-milled cellulose at different times, (a) Ball-milled cellulose at 30 min, (b) Ball-milled cellulose at 60 min, (c) Ball-milled cellulose at 90 min and (d) Ball-milled cellulose at 120 min

X-ray diffraction (XRD): Measurements are shown in Fig. 5, showing the XRD of the different ball milling samples at different milling time durations. The XRD patterns correspond to the ball-milled cellulose at different times. The degree of crystallinity was calculated using the following Eq.:

$$\text{CI}\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100$$

where I_{002} is the intensity of the region of crystalline cellulose (2θ = 22.4°) and I_{am} is the intensity of the amorphous region (usually around 2θ = 18.5°)[28]. The raw material has a diffraction peak around 2θ = 22.5 and the amorphous region was slightly intense, indicating type I cellulose and the figure well shows that the intensity of crystalline cellulose decrease as the ball-milling duration time increases. This is attributed to the deformation under the ball milling effect over some time. We have noticed that the colour of the obtained cellulose is getting darker and this is due to contamination from balls or vial walls. Compared to other study[29] the crystallinity degree of the resulting nanofibers was higher than the extracted cellulose.

The XRD analysis showed that the crystallinity degree of nano-cellulose was higher than cellulose in the amount of 76.01%.

Scanning electron microscopy (SEM): The morphological structures of the different cellulose and nanoscale samples are shown in Fig. 6a-e, Fig. 6a display the morphological structure of the raw cellulosic material (before milling), the figure well shows the structure of cellulosic fibrils before milling out of nanoscale. The data in Fig. 6b-e show the significant change in the fibre after ball milling. The ratio of sample to balls and balls sizes were fixed according to some previous works[17]. The figures show a significant appearance for cellulose nanofiber. The figures revealed that the greater the milling time, the greater the homogeneity of the fibres and remarkable homogeneity well appear at higher ball milling duration of time.

Thermogravimetric analysis (TGA): Curves are shown in Fig. 7 shows the thermogravimetric behaviour of different

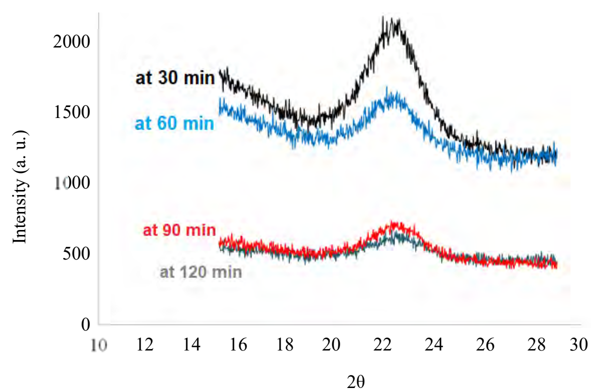

Fig. 5: XRD patterns of ball-milled cellulose

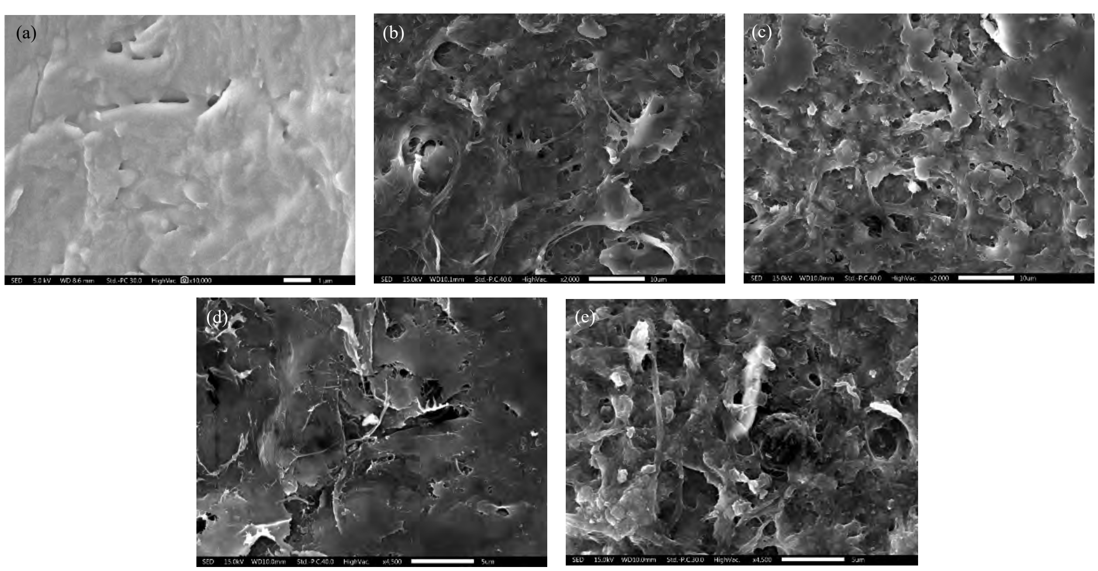

Fig. 6(a-e): SEM images of (a) Cellulose, (b), (c), (d), and (e) are ball-milled cellulose at 30, 60, 90 and 120 min, respectively

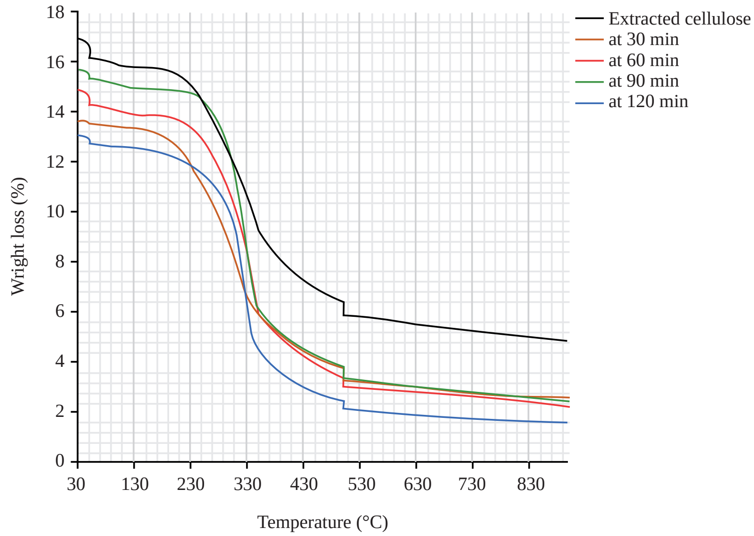

Fig. 7: TGA curves for all samples

samples. It displays degradability and thermal stability. The figure shows that all the samples in a low reduction of mass before 100°C, which is attributed to loss of low molecular weight substances. The curves show a great similarity in the weight loss of ball-milled samples. This may be attributed to the similarity of conidiation (grinding process). However, the ground samples show characteristic thermal behaviour, which is different from the raw material, as the cellulosic raw material does not modify. The main mass loss takes place at a temperature range from 230-430°C, which is related to the deformation of cellulosic material. In general, the thermal behaviour of the samples is by the date in cited references and the thermal degradation of the almost ground samples are different from the raw cellulosic material.

This study will help in using the ball milling technique for the production of cellulose nanofibers from date-palm tree wastes as local biomass without using any hazardous chemicals and provide meaningful and effective guidance for mass production.

CONCLUSION

Cellulose can be extracted from the date-palm tree at a good yield. Ball milling was found as an effective process to transfer the extracted cellulose into nanofibers (CNFs), the milling time is a significant parameter in the process and the optimal time for obtaining cellulose nanofiber was 120 min for mild basic treatment cellulose. This study discovers the simple eco-friendly approach that can be beneficial for converting the local agriculture wastes into value-added materials such as nano-cellulosic fibres. We strongly recommend recycling the wastes from date-palm trees into value-added materials like nanocellulose.

SIGNIFICANCE STATEMENT

This study describes the extraction of value-added materials from the local environmental biomass that can be beneficial for recycling the date-palm tree wastes and utilizing them in industry. The information reported herein will help the local authorities and research centres to find proper ways and eco-friendly approaches for recycling date-palm trees by-products. It is important to note several important applications of nanocellulose crystals and fibres in the industries. Thus, there is a new contribution to knowledge with regards to the nanocellulose applications as well as its ability to bind with other materials for water treatment and water purification.

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