Al-Imam Muhammad ibn Saud Islamic University
College of Science
Department of Chemistry

Preparation of Nano particles of Saudi Bentonite and Cellulose.

A graduation research project submitted to the Department of Chemistry in partial fulfilment of the requirements for the completion of the degree of

Bachelor of Science in ***Chemistry***.

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Contents

Acknowledgment

All praises are due to Allah (SWTA), and we ask Allah for acceptance, forgiveness, and well-being in this world and the hereafter. We also ask Allah for a good end and a favorable outcome. Since the beginning of creation, humans have sought knowledge, driven by curiosity and a love for learning and understanding the unknown. From that time until today, humanity has gathered an immense amount of information and facts. With the passage of time, humans began conducting experiments and research to uncover the secrets and hidden truths of everything unfamiliar. In this spirit, our research compiles the most important experiments, facts, and secrets, as well as the most significant information and details about **Nano particles of Saudi Bentonite and Cellulose**. We hope that our research will be among the approved and reliable works that benefit every lover of knowledge and science.

All thanks and praise are due to Allah (SWT), the Lord of all things, for enabling us to complete our research successfully. We also extend our gratitude to our parents for their efforts, for granting us the opportunity, and for providing us with the means to achieve this. Furthermore, we would like to thank **Dr. Abdulrahman Alhamazani** for his efforts and assistance throughout this project. We hope that we have succeeded in clarifying all the information and that our work will be a valuable contribution to the field.

Abstract:

In this graduation project, we used Bentonite Clay In Three Different Ways to obtain nano-particles of bentonite. The First Method is Sonication, In Which We Used Bentonite With Ethanol At Four Different Times, And The Second Method is using Planetary Ball Milling technique, In Which We Used Two Methods, A Dry Sample And A Wet Sample Using Water. The Third Method, we used Solvothermal method to obtain nanoparticles of bentonite. We Used Bentonite With ethanol in autoclave. In contrast, we have succefully extracted cellulose from wastes of date-palm trees by collecting dry fronds and subjected to steps of chemical treatment to obtain cellulose.

الملخص باللغة العربية

لقد قمنا بتحويل عينات بنتونايت محلية الى نانو بنتونايت. وقد قمنا بعمل خطوات عملية لتحويل طين البنتونايت الى جزيئات نانوية اول هذه الطرق جهاز الموجات فوق الصوتية وقد استخدمناه في عدة أوقات مختلفة , والطريقة الثانية كانت عباره عن طاحنة الكور واستخدمناها في ظروف مختلفة عينات جافه وعينات رطبه , والطريقة الثالثة كانت عباره عن جهاز مفاعل الاوتوكليف الحراري المائي .

وقد قمنا باستخراج السليلوز من مخلفات أشجار النخيل عن طريق خطوات من المعالجات الكيميائية كيميائية بدء من استخدام جهاز لتبريد وتكثيف الابخرة في السوائل . وانتهاء بتميوء العينة باستخدام مواد قلوية وفي أوساط مختلفة.

1. Introduction:

Bentonite:

Bentonite is an off-white montmorillonite clay formed from altered volcanic ash. It has a sheet-silicate structure and is especially notable for the way in which it absorbs and loses water and for its base-exchange properties. Sodic bentonite can absorb up to 10 times its own weight in water and can swell to 18 times its dry volume. Thus, it can be applied where its colloidal properties can be exploited. Bentonite has a wide variety of uses including foundry, animal feed, drilling mud, absorbent, industrial, and specialty uses. [1]

Date-Palm trees:

For palm tree Synthetic fibers, because of their high stiffness and strength, are widely used in the textile industry as well as in composites. However, these fibers show some disadvantages in terms of biodegradability, processing costs, recyclability, energy consumption, and machine abrasion. Thus, there has been an increased interest in production and use of natural fibers for textiles and composites. Natural fibers have accompanied human societies since prehistoric times. However, during the 20th century, the production of cheap petroleum-based fibers has nearly destroyed the production and utilization of natural fibers such as hemp and flax in the western countries. Recently, environmental concerns and the growing global waste problem have spurred much research into the development of bio-based materials and motivated governments to increase the legislation pressure. The advantages of plant fibers over synthetic ones include their low cost, light weight, local availability, and their outstanding [2]

There are three main types of Cellulose structure: triclinic Iα,monoclinic I and cellulose II. Depending on the purpose of cellulose using, structural parameters are of critical importance. Besides purity (amount of residual lignin), crystallinity index (CI), crystallite size(determined by CSR) and degree of polymerization (DP) seems to be key parameters. These settings affect the order of cellulose structure, and hence the properties of the resulting material.[3]

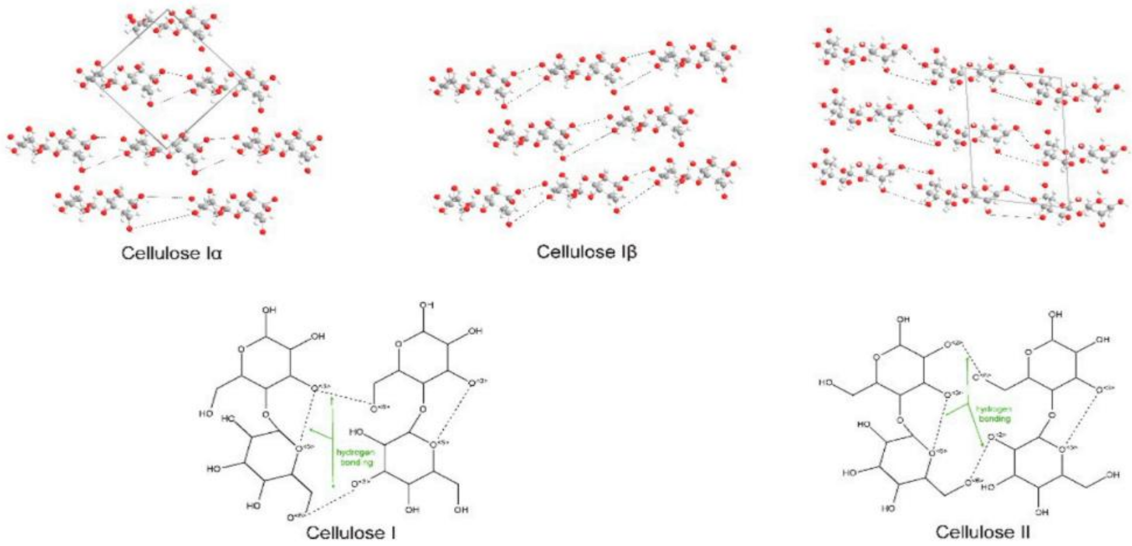

Figure 1. Three main structures of Cellulose

Properties and structure of Bentonite

European Bentonite Association (EUBA) well-defined 4 types of Bentonite qualitatively: calcium bentonite, natural sodium bentonite, and acid-activated Bentonite. organophilic bentonite. The following figure (2) shows the types of bentonite.

Figure 2. Photos of type of Bentonite, (A) Calcium Bentonite, (B) Natural sodiutm Bentonite, (C) acid-activated Bentonite (D) organophilic bentonite [4]

Calcium Bentonite is a type that is mainly full of Ca^{2+} or Mg^{2+} ions in the middle layers. Natural Sodium Bentonite is generally Wyoming Bentonite, although it is found in other locations as well. Na Bentonite is mostly filled by Na^{2+} ions in the middle layers. Ca^{2+} or Mg^{2+} ions can also happen, usually in Sodium bentonite in changeable concentrations. Activated Bentonite has the primary composition of Ca^{2+} ions in the middle layer exchanged with Na^{+} ions during a technical process known as alkali activation. Acid-activated Bentonite is a type of Bentonite with a structure that has been partly dissolved by acid treatment. Based on the degree of activation, original Na^{+}, Ca^{2+}, and Mg^{2+} cations are mostly removed, and parts of Si, Al, Mg, and Fe from the framework are dissolved. Acid-activated Bentonite shows a high surface area above 200 m^2/g and a large microspore volume, making it an excellent absorbent. Organophilic Bentonite or organoclays contain cations in the middle layers exchanged by polar organic molecules. They are hydrophobic, and they can swell in organic solvents. [5]

Chemical composition in %			
	Wyoming "Volclay"	Panther Creek Mississippi	Ponza, Italy
Silica, SiO_2	64.32	64.00	67.42
Alumina, Al_2O_3	20.74	17.10	15.83
Ferric oxide, Fe_2O_3	3.03	} 4.70 {	0.88
Ferous oxide, FeO	0.46		-
Titanium dioxide, TiO_2	0.14	1.50	-
Lime, CaO	0.50	3.80	2.64
Magnesia, MgO	2.30	0.50	1.09
Potash, K_2O	0.39	0.20	}1.09
Soda, Na_2O	2.59	-	
Phosphoric anhydride, P_2O_5	0.01	-	-
Sulfuric anhydride, SO_3	0.35	0.20	0.01
Other minor constituents	0.01	8.00	-
Combined water	5.14	64.00	10.88

Figure 3. Chemical Composition of Bentonite. [6]

Uses of bentonite

1. Drilling mud

Bentonite is used in drilling fluids to lubricate and cool the cutting tools, to remove cuttings, and to help prevent blowouts. Much of bentonite's usefulness in the drilling and geotechnical engineering industry comes from its unique rheological properties. Relatively small quantities of bentonite suspended in water form a viscous, shear-thinning material. Most often, bentonite suspensions are also thixotropic, although rare cases of rheopectic behavior have also been reported. At high enough concentrations (about 60 grams of bentonite per litre of suspension), bentonite suspensions begin to take on the characteristics of a gel (a fluid with a minimum yield strength required to make it move). So, it is a common component of drilling mud used to curtail drilling fluid invasion by its propensity for aiding in the formation of mud cake. [7]

2. Binder

Bentonite has been widely used as a foundry-sand bond in iron and steel foundries. Sodium bentonite is most commonly used for large castings that use dry molds, while calcium bentonite is more commonly used for smaller castings that use “green” or wet molds. Bentonite is also used as a binding agent in the manufacture of iron ore (taconite) pellets as used in the steelmaking industry. Bentonite, in small percentages, is used as an ingredient in commercially designed clay bodies and ceramic glazes. Bentonite clay is also used in pyrotechnics to make end plugs and rocket engine nozzles.

The ionic surface of bentonite has a useful property in making a sticky coating on sand grains. When a small proportion of finely ground bentonite clay is added to hard sand and wetted, the vi clay binds the sand particles into a mouldable aggregate known as green sand used for making Molds in sand casting. Some river deltas naturally deposit just such a blend of clay silt and sand, creating a natural source of excellent Molding sand that was critical to ancient metalworking technology. Modern chemical processes to modify the ionic surface of bentonite greatly intensify this stickiness, resulting in remarkably dough-like yet strong casting sand mixes that stand up to molten metal temperatures. [7]

The same effluvial deposition of bentonite clay onto beaches accounts for the variety of plasticity of sand from place to place for building sand castles. Beach sand consisting of only silica and shell grains does not mold well compared to grains coated with bentonite clay. This is why some beaches are much better for building sand castles than others.

The self-stickiness of bentonite allows high-pressure ramming or pressing of the clay in molds to produce hard, refractory shapes, such as model rocket nozzles. To test whether a particular brand of cat litter is bentonite, simply ram a sample with a hammer into a sturdy tube with a close-fitting rod; bentonite will form a very hard, consolidated plug that is not easily crumbled. [7]

3.Purification

Bentonites are used for decolorizing various mineral, vegetable, and animal oils. They are also used for clarifying wine, liquor, cider, beer, and vinegar.

Bentonite has the property of adsorbing relatively large amounts of protein molecules from aqueous solutions. Consequently, bentonite is uniquely useful in the process of winemaking, where it is used to remove excessive amounts of protein from white wines. Were it not for this use of bentonite, many or most white wines would precipitate undesirable flocculent clouds or hazes upon exposure to warm temperatures, as these proteins denature. It also has the incidental use of inducing more rapid clarification of both red and white wines. [7]

4. Absorbent

Bentonite is used in a variety of pet care items such as cat litter to absorb the odour and surround the faces. It is also used to absorb oils and grease. [7]

5. Groundwater barrier

The property of swelling on contact with water makes sodium bentonite useful as a sealant, since it provides a self-sealing, low-permeability barrier. It is used to line the base of landfills to prevent migration of leachate, for quarantining metal pollutants of groundwater, and for the sealing of subsurface disposal systems for spent nuclear fuel. Similar uses include making slurry walls, waterproofing of below-grade walls, and forming other impermeable barriers, e.g., to seal off the annulus of a water well, to plug old wells. [7]

Bentonite can also be “sandwiched” between synthetic materials to create geosynthetic clay liners (GCLs) for the aforementioned purposes. This technique allows for more convenient transport and installation, and it greatly reduces the volume of bentonite required. It is also used to form a barrier around newly planted trees to constrain root growth so as to prevent damage to nearby pipes, footpaths and other infrastructure. Farmers use bentonite to seal retention ponds. [7]

6. Medical

Bentonite has been prescribed as a bulk laxative, and it is also used as a base for many dermatologic formulas. Granular bentonite is being studied for use in battlefield wound dressings. Bentonite is also sold online and in retail outlets for a variety of indications. Bentoquatam is a bentonate-based topical medication intended to act as a shield against exposure to urushiol, the oil found in plants such as poison ivy or poison oak.

Bentonite can also be used as a desiccant due to its adsorption properties. Bentonite desiccants have been successfully used to protect pharmaceutical, nutraceutical, and diagnostic products from moisture degradation and extend shelf life. In fact, in the most common package environments, bentonite desiccants offer a higher adsorption capacity than silica gel desiccants. Bentonite complies with the FDA for contact with food and drugs. [7]

Preparation of bentonite:

A weathered bentonite was altered by mechanochemical mixing with sodium carbonate to give sodium type bentonite. The product was purified by conventional dispersion-sedimentation method to obtain purified sodium bentonite. The altered acid clay and the purified product exhibited useful swelling properties. An organophilic clay was prepared by the ion exchange of the purified product with a cationic surfactant. [8]

Source of Bentonite in Kingdom of Saudi Arabia:

Bentonite, found in the region of Saudi Arabia that we engage in, is formed by the solidification of the molten state. It is believed to have been formed millions of years ago, possibly from volcanic ashes falling in stagnant salted water in semi-arid conditions with 18-20 inches of annual rainfall. [9]

2. Literature Review:

Bentonite:

In a reported study by El-Nagar, D & Sary, D, [10] aiming to assess the influence of bentonite and nano bentonite application on the physical and chemical properties of sandy soils. They, prepared Nano-particles of bentonite were by Sonochemical,and bentonite and nano bentonite were characterized by (XRD), (XRF), (AFM), surface area and (FTIR). They found that the Nano bentonite had abundance of montmorillonite than did raw bentonite. The surface area of nano bentonite increased compared to that of raw bentonite. The obtained results revealed that the addition of nano bentonite improved water characteristics of soil such as: available water and water holding capacity. Results showed that T4 treatments significantly increased the biological yield, grain yield and (100-grain). [10]

In another study by Mahmoud, he successfully prepared and characterized nano-bentonite for anionic dye removal (DY 50). He used X-Ray Diffraction (XRD), X-ray Fluorescence (XRF), Scanning Electron Microscope (SEM), EDAX analysis, FT-IR, and TGA for characterization. The obtained results indicated the formation of nanoparticles with an average size of 15 nm. The effect of different operating conditions was studied using different pH, dose, contact time, temperature, and initial DY 50 concentrations. The obtained results indicated that nano bentonite was able to adsorb about 78.3 and 100% for initial concentrations of 100±8.1 and 20 ±1.62 mg/L, respectively. The optimum removal conditions were observed at acidic media (pH 3) using sorbent material dosage 1 g/L for 45 min and 30°C. The adsorption isotherm, kinetic analysis, and thermodynamic behavior were studied by using linear equation form, and the adjusted R2 was compared to detect the preferred models. [11]

In the another study by Nurdin Bukit, 2013 Chemistry & Material Research

The Objective of this study is the preparation of natural bentonite in nano particle material as filler and reinforcement of thermoplastic high-density polyethylene (HDPE) that has mechanical properties and good thermal properties and can be used as one component in the automotive industry. The method is performed in the preparation of nano particles is done by purification with HCl solution, calcination at a temperature of 600 C for 2 hours and the ball mill for 10 hours to get natural bentonite nanometers in size and materials used as a filler thermoplastic HDPE. The results particle size Analyzer (PSA) average diameter of the particles 97.5 nm, with the X-rays diffraction (XRD) obtained by means of an average particle size of 49.80 nm and the highest content of EDX analysis on natural bentonite is aluminum (Al) and silicon (Si). with the X-rays diffraction analysis obtained from natural Bentonite is a kind of aluminum silicate mineral and classified types of Wyoming (Na- bentonite). The minerals present in the clay consists of a group of minerals cristobalite quartz, mica group minerals from the annite, analcime from feldspar group minerals, and mineral carnegieite of feldspathoid group. The biggest content of samples of clay minerals crystoballite this phase is about 68%, while the result of nano composite (HDPE blend natural bentonite nano particle) with XRD analysis occurs intercalation between nano bentonite with HDPE, thermal analysis were shown enthalpy increased with increasing nano composites bentonite particles, the results of the mechanical properties of nano composite in an increased of the maximum tensile strength on quantity of 2 to 6 wt%, and a decline in the larger quantity of 6 % wt and a decrease in elongation at break with the addition of nano-particles of natural bentonite from SEM analysis HDPE blend with nano bentonite is homogeneous.[12]

Date-Palm Trees:

Study By Journal Of Renewable Materials , 2019 , A Date palm (phoenix dactylifera), which is mostly found in the middle east countries such as Iran, Iraq, Saudi Arabia, and the United States (California) that play a significant role in the economical and the environmental condition in those areas. The main purpose of planting dates is its fruit, which is consumed as fresh, dried or processed forms. There are approximately 100 million date palm trees in the worldwide that 62 million of these trees located in the Middle East and North Africa. In Saudi Arabia only, 15000 tons of date palm leaves is prepared as waste materials. The leaves of date palm tree are used in several applications such as making ropes, baskets, and mats in many parts of the world. Unfortunately, the huge amount of the non-food products from the date palm remains as landfill materials without any specific usage. By attention to the date palm properties, the literature clearly showed that each part of date palm has great potential to be used for a variety of applications such as: making paper, absorption of heavy and toxic metals, energy production and soil fertilizing. Some of the obstacles and solutions for using palm date in these applications were also explored. Considering these issues and their solutions, the date palm is a favourable alternative. Despite some limited and traditional uses of these palm wastes, this review considered date palm applications and the properties' of the most important part of that tree in recent researches and related issues for future research are also spotted. [13]

Another Study By Soumya Koippully Manikandan, Dharshini Jenifer. A, Nisarga K. Gowda, Vaishakh Nair, Rami Al-Ruzouq, Mohamed Barakat A. Gibril, Fouad Lamghari, John Klironomos, Maryam Al Hmoudi, Mohamed Sheteiwy, Ali El-Keblawy, Date palm (*Phoenix dactylifera* L.) cultivation in the Arabian Peninsula is crucial for regional agriculture and global markets. The Arabian Peninsula is dominant in date production, contributing approximately 34 % of the global output. Recent advancements in agricultural technologies have improved fruit yield and quality, expanding date palm cultivation globally. However, sustainability challenges persist due to various abiotic stresses, such as salinity, temperature extremes, drought, soil factors, and biotic stresses, including diseases and pests. This review examines key environmental factors affecting date palm cultivation, with a focus on soil salinity, water scarcity, and climate change-related stresses. The genetic diversity among date palm varieties is emphasized, highlighting the need for breeding programs aimed at improving stress tolerance and yield. Biotechnological advancements, such as genetic transformation and genome editing, are discussed for their potential to enhance crop resilience and productivity. Additionally, remote sensing techniques are explored for their application in precision agriculture, particularly in the mapping and monitoring of date palm health and soil conditions. The significant role of artificial intelligence in accurately mapping date palm trees using multi-platform remotely sensed data is also reviewed, illustrating its potential to enhance geospatial databases and support sustainable management practices. The review concludes with recommendations for optimizing cultivar selection and management strategies tailored to local conditions, emphasizing the need for ongoing research to advance date palm cultivation on a global scale. [14]

And Another Study By Nour El Bana , Date palm trees are grown for its fruit and are the oldest cultivated tree fruits. The fruits known as dates are sweet and highly nutritious fruits. The major producers of date palm trees are countries in the Middle East and other countries in Africa while Iran is the largest exporter. Date palm trees are cultivated in dry arid zones having irrigation facilities. Date farming can have a successful cultivation in regions that have prolonged hot dry summer, moderate winter climatic conditions with no rain during the fruit ripening period. Date trees grow about 65 to 70 feet (20 to 21 m) in height. The trunk is cylindrical and columnar growing straight with the same girth to the top. Date palm is a dioecious tree which means the male (staminate) and female (pistillate) flowers are born on two different palm trees. The fruits are one to four centimetres long with 2.5 cm diameter, oblong in shape. The fruits are one-seeded and are fleshy. The trees are well adapted to desert environmental conditions. They can survive extreme temperatures and water scarcity. Fruit yield gets affected by fruit cracking and checking, due to moisture presence, hence low humidity is preferred at the fruit development stage. Date farming can be carried out on a wide range of soils with varying amounts of soil mineral nutrients and organic matter. The trees can tolerate saline soils. The trees are found to grow in all the five continents. Most farmers follow traditional methods in date farming with no proper tree and fruit bunch management. This leads to the production of low fruit quality yield. Application of fertilizers, pruning, and fruit thinning will yield quality fruits which will have great market value. Nowadays, many people are showing interest in Date palm cultivation in India. Already there are many Dates Orchards established in Tamil Nadu, Karnataka, Andhra Pradesh, Gujarat, Maharashtra, and Rajasthan. [15]

Cellulose Extraction:

There are several works regarding extraction of cellulose from agriculture waste. In this study, authors have reported series of operations to isolate the micro-cellulose from the palm tree spathe sheath by using a modified chemical method to take into account the low cost and the completion speed and its characterization using X-ray diffraction technique (XRD), infrared spectroscopy (FTIR) and scanning electron microscope coupled with element analyzer (SEM/EDX). The results showed that the extraction method succeeded in obtaining very pure microscopic fibers with a width of 2–10 μm with a crystallinity index equal to 79.
in this research, a modified chemical method for the isolation of cellulose Iβ and II from spathe sheath was reported. The results proved that the crystallinity index can be improved by increasing acidic hydrolysis time. [16] In another study of cellulose, Towards the utilization of different parts of date palm biomass waste, low-concentration acid-alkali treatment was used to isolate the contained cellulose and α-cellulose. The cellulose yields achieved from the rachis, leaflet, and fiber parts of the biomass were 74.70%, 71.50%, and 73.82%, respectively, while the corresponding α-cellulose yields were 78.63%, 75.64%, and 70.40%, respectively. The cellulose samples were bleached and characterized by thermogravimetric analysis (TGA),

Fourier-transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). The XRD results revealed high crystallinity of both the cellulose and α-cellulose samples, while the TGA thermograms indicated that the alkali treatment completely removed lignin and hemicelluloses from the rachis. The results of this study demonstrate the promise of using date palm biomass waste as raw material to produce cellulose and α-cellulose. Low-concentration acid-alkali treatment and bleaching were successfully used to isolate cellulose and α-cellulose from different parts of lignocellulosic date palm waste, namely, rachis, leaflet, and fiber. The non-cellulosic fractions of the date palm biomass (hemicellulose and lignin) were removed in the process. The rachis part yielded the highest amounts of cellulose and α-cellulose, as attested to by both the experiments and statistical design. The characterization of the α-cellulose obtained from rachis revealed properties similar to those of commercial α-cellulose. [17]

And another study of cellulose, TY - JOUR , Isolation and Characterization of Cellulose Nanocrystals from Date Palm Waste, AU - Raza, Mohsin, AU - Abu-Jdayil, Basim, AU - Banat, Fawzi, AU - Al-Marzouqi, Ali H , 2022. This study presents the isolation, characterization, and kinetic analyses of cellulose nanocrystals (CNCs) from date palm waste in the United Arab Emirates. After bleaching date palm stem waste with acidified $NaClO_2$ and delignification via NaOH treatments, cellulose was extracted. Mineral acid hydrolysis (62 wt % H_2SO_4) was performed at 45 °C for 45 min to produce crystalline nanocellulose. Fourier transform infrared (FTIR) and chemical composition analysis confirmed the removal of no cellulosic constituents. The crystallinity index increased gradually with chemical treatments, according to the obtained X-ray diffraction (XRD) results , Cellulose nanocrystals were successfully isolated from date palm waste, which is the most abundant biomass available in the UAE. CNC was produced through the following steps: bleaching, delignification, and acid hydrolysis. The removal of lignin and hemicellulose after bleaching and delignification was confirmed via chemical composition analysis and FTIR spectra. [18]

Experimental Section:

1. Materials,

Saudi Bentonite, this sample was obtained from Khalais area in Jeddah city. Ethonal (high pure), Distilled water. Date-Palm tree fronds were collected from local farm in Riyadh city , and ammonium molybdate , distilled Water , H2o2 (34.01M) , NaOH (0.15M) Na2SiO3 , NaClO2 acetic acid

2. Preparation of Nano-Bentonite

2.1. Using ultrasonication bath:

We took 0.2 grams of bentonite and added 60 mL of ethanol. Then, we stirred the mixture for 15 min to obtain homogenous solution and we put it in ultrasonic bath for 4 samples in different time 30 min , 60 min , 180 min , 240 min. After, we filtrated the mixtures using Buchner funnel under vacuum. Then, we dried the samples in oven at for 1 hour at 110^{o} C. then, we crushed the particles and put them into the crucibles, and we placed them into oven at 590o C for 3 hours. then save sample in small plastics vials (Eppendorf) for characterization and measurements.

2.2. Using Planetary Ball Mill Machine:

First Sample: 1 g of bentonite was placed into ball-mill vial, then we added 50.7 g balls. The time was 1 hour and the speed of rotation was 400 rpm. At the end, we collected the sample in small plastic tube (Eppendorf) .

Second Sample: 1 g of bentonite was placed into ball-mill vial, then we added 50.7 g balls, we added 15 distilled water. The time was 1 hour and the speed of rotation was 400 rpm. At the end, we filtrated the solid, then dried in oven.

Third sample: We took 5g of bentonite, and 50.7 g of Balls were added. We started the ball-milling 12 hour at 400Rpm rotation speed, then we Saved the sample in small plastic, (Eppendorf) .

2.3. Using solvothermal:

In Teflon, we Added 1 g bentonite and 100 ml ethanol, then we stirred the mixture for homogenous solution for 5 min at 5 rpm. Then, we transferred the Teflon beaker in autoclave, and placed in oven at 170^{o} C for 24 hours. Then we used funnel filtration and dry the solid, we take the sample and save in small plastic(Eppendorf) for characterization and measurements.

Ultrasonic Autoclave oven Ball mill

Figure 4. Photos of the experiment apparatuses.

3. Preparation of Cellulose from Date-Palm tree waste:

We took 8 g ammonium molybdate and dissolve 100 ml distilled water , after we use6 ml H2O2 To reach PH(4) , And Fill to 50 ml , we mix the solution with fronds 10 g , we put in funnel flask the solution and stirrer on hot plate for 1 hour , after 1 hour we cooling the mixture , then in funnel flask add NaOH 3g and 3ml H2O2 and 2g Na2SiO3 then stirring 1hour 70-80 temperature then filtration and drying , take the sample in beaker with NaClo2 with acetic acid and stirring and wait for reach the temperature 80 c then calculate 1 hour , then cooling and add distill water to stop the reaction , decantation 3 time by distilled water ,leave it to dry.

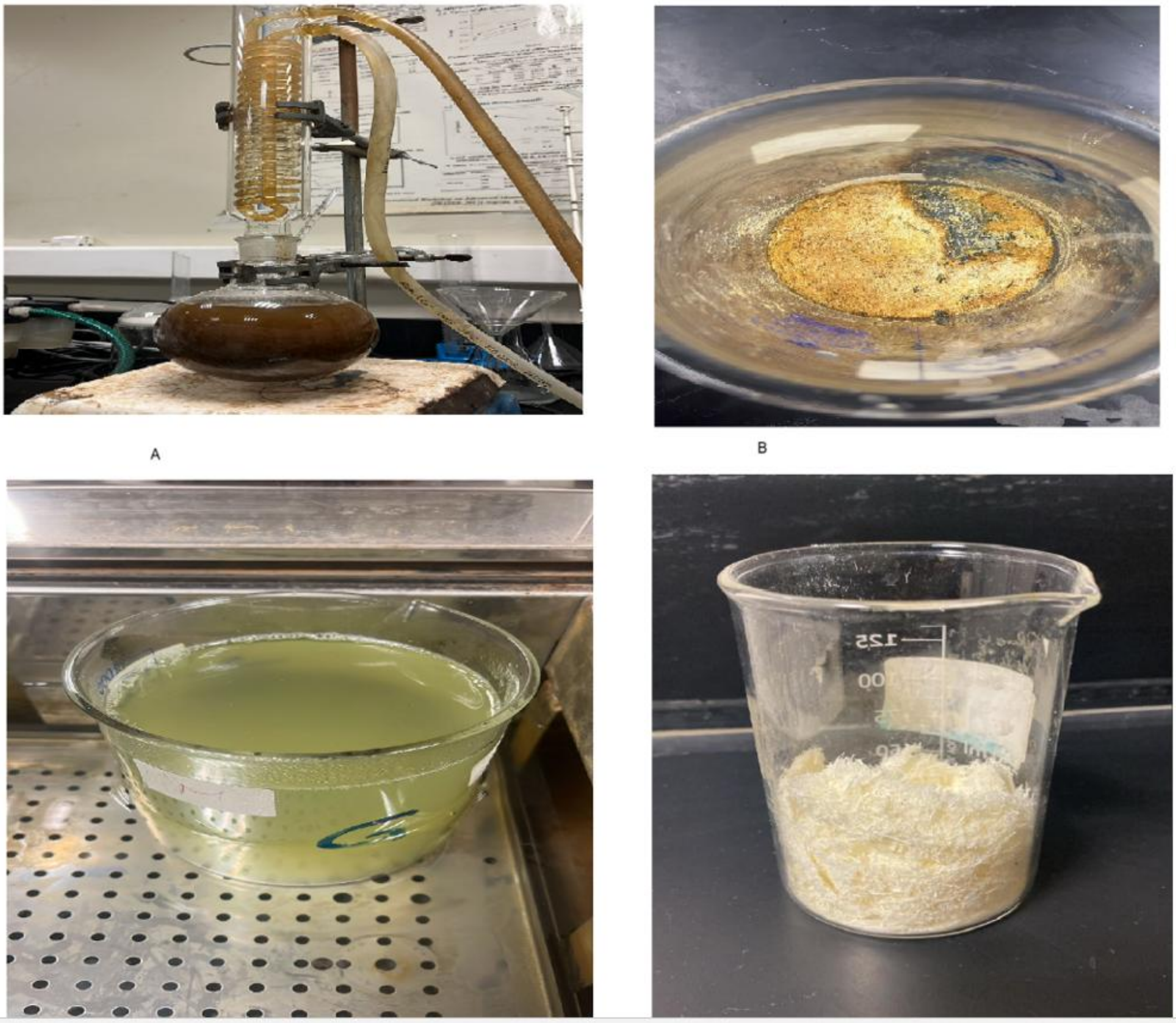

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Figure 5. (A) the Condenser step , (B) Date-palm tree with molybdate , (C) molybdate with NaClO2 and acetic Acid (D) Cellulose after use Mo , NaOH , ClO2.

3. Results and Discussion:

The following table illustrates the samples numbers and the conditions that have been done for the preparation.

Table 2. Sample of Bentonite

#Sample	Method	Conditions
1	Sonication	0.2g bentonite 60 mL ethanol, 30 min sonication, 590 ºC calcination
2	Sonication	0.2g bentonite 60 mL ethanol, 60 min sonication, 590 ºC calcination
3	Sonication	0.2g bentonite 60 mL ethanol, 180 min sonication, 590 ºC calcination
4	Sonication	0.2g bentonite 60 mL ethanol, 240 min sonication, 590 ºC calcination
5	Solvothermal	1g bentonite , 170 ºC , 100 ethanol , 24 hour , autoclave
6	Ball milling	1g bentonite , 13 balls , 1 hour , 400rpm , dry
7	Ball milling	4g bentonite , 13 balls , 1 hour , 400rpm ,15ml H2O , wet , centrifuge filtration
8	Ball milling	4g bentonite , 13 balls , 1 hour , 400rpm , 15ml H2O wet , funnel filtration
9	Ball milling	5g bentonite , 13 balls , 12hour , 400rpm , dry

Then, the samples were measured by Fourier Transform infrared (FTIR) and Scanning Electron Microscopy (SEM). The following pictures are the SEM and EDS measurements of bentonite samples.

Figure 6 shows the Energy Dispersive Spectroscopy (EDS) results of nanobentonite sample #4. It typically provide elemental composition data, including the mass percentages of carbon (C), oxygen (O), Magnesium (Mg), Aluminum (Al), silicon (Si), potassium (K), calcium (Ca), titanium (Ti), and iron (Fe).

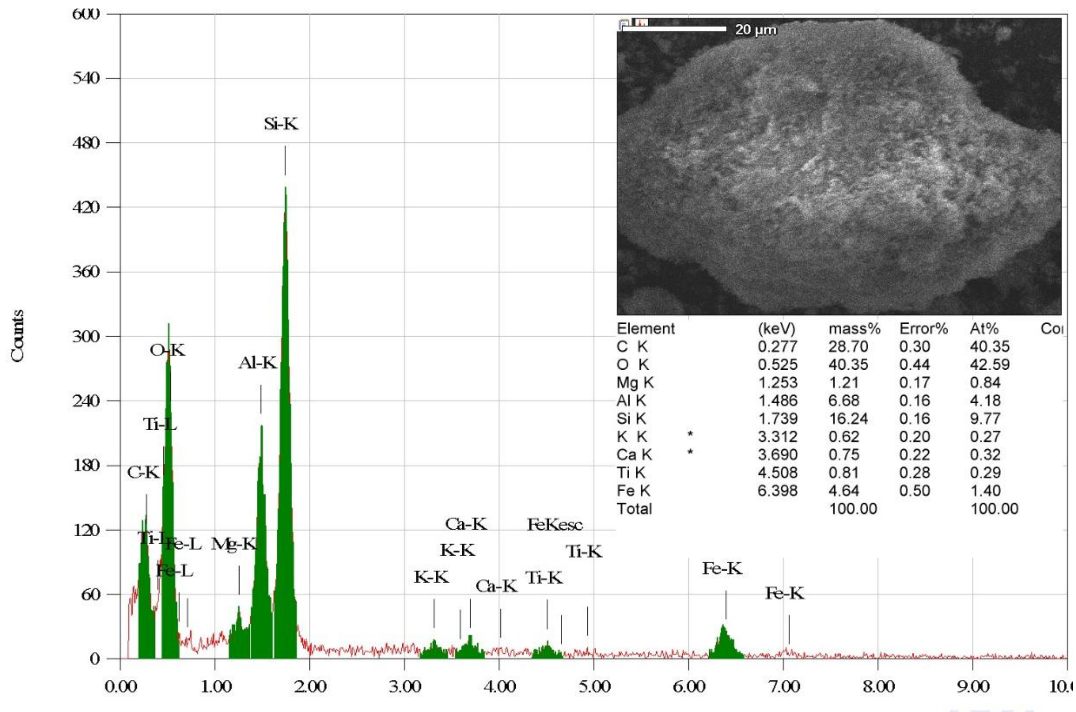

Figure 6. SEM-EDS analysis of sample #4

These elements indicate that presence of carbon in nanobentonite can be attributed to organic impurities, residual carbon from synthesis or modification processes, or contamination from the environment. In some cases, carbon might also appear due to sample preparation (e.g., carbon coating for conductivity in SEM-EDS analysis). Oxygen (O) Mass% is a major component of nanobentonite as it is part of the silicate structure. The high O mass% is mainly due to the presence of SiO_2 (silica) and aluminosilicate minerals, which are the primary constituents of bentonite. It might come from the hydroxyl groups or water molecules are present, they can contribute to the oxygen content as well. Silicon (Si) Mass% is the third major component of the sample, and it is a key element in the bentonite structure, primarily existing as SiO_2. A high Si mass% confirms the presence of the tetrahedral silica framework of montmorillonite, the main mineral in bentonite. The Si/O ratio can indicate the purity of the silicate structure—variations might suggest the presence of impurities or modifications.

The C mass % is 29% suggests surface modification or contamination. Also, A high O mass% is expected due to silicates but can also indicate oxidation or hydration. A high Si mass%

supports the purity and presence of the silica framework. Comparing the Si/O ratio with theoretical values for SiO_2 or aluminosilicates can help assess the composition and potential impurities.

Scanning Electron Microscopy (SEM) of samples 4, 5, 7, and 9 are showing in the following figures 7, 8, 9, and 10, respectively.

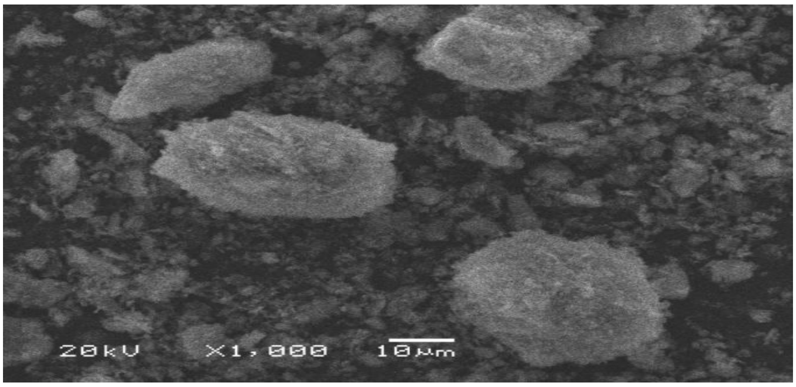

Figure 7. Bentonite in sonication and ethanol sample #4

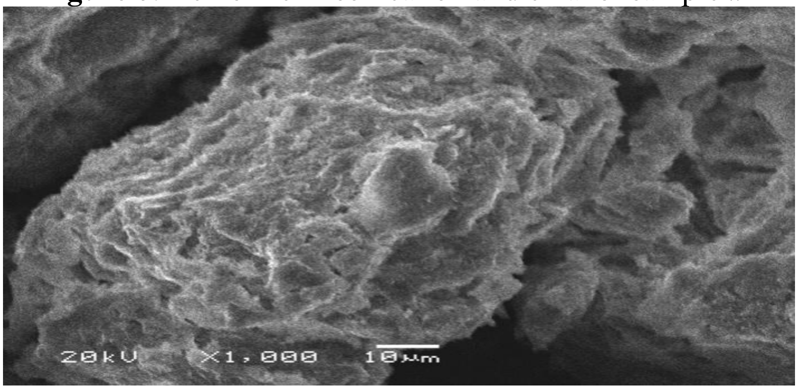

Figure 8. Bentonite in solvothermal and ethanol sample #5

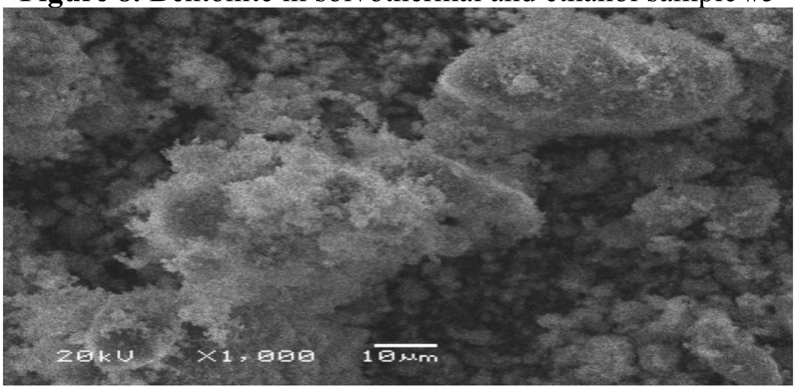

Figure 9. Bentonite in ball milling 60min sample #7

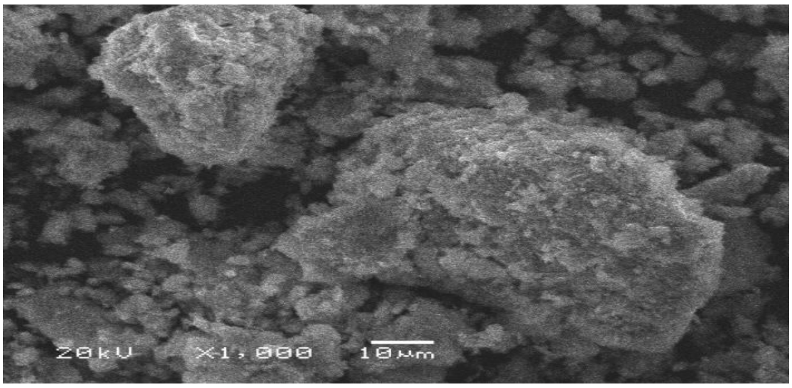

Figure 10. Bentonite in ball milling 12-hour sample #9

The SEM images of bentonite prepared using sonication, solvothermal, wet ball milling, and dry ball milling suggest that the processing methods have influenced particle size and morphology. The potential differences in micro and nano structure based on these methods are discussed on the following:

1. Sonication: Sonication helps break down large agglomerates by applying ultrasonic waves, leading to exfoliation and dispersion. The resulting particles often have irregular and flaky shapes, with a tendency to form thin sheets due to the layered silicate structure of bentonite. If the observed size is still around 10 µm, it suggests incomplete delamination or re-agglomeration after drying.

2. Solvothermal: The solvothermal method involves high-pressure and temperature conditions, promoting crystal restructuring and possible phase changes. Particles obtained might have more uniform morphology with enhanced porosity, depending on the solvent and reaction time. The presence of rounded or well-defined edges could indicate recrystallization effects.

3. Wet Ball Milling: This method involves milling bentonite in a liquid medium, reducing particle size through mechanical grinding and shear forces. It often results in smaller, more uniform particles with reduced agglomeration compared to dry milling. If 10 µm particles are observed, it could mean that either the milling duration was insufficient or that bentonite's plate-like structure resists further size reduction beyond a certain limit.

4. Dry Ball Milling: Dry milling applies mechanical force without a liquid medium, leading to larger and more irregularly shaped particles compared to wet milling. This process can cause higher agglomeration and generate rougher surface textures due to particle-particle interactions.

If 10 µm sizes are still observed, it may indicate a balance between fracture and agglomeration during milling. In the other hand, the Sonication likely results in thin, sheet-like structures. Solvothermal may show more rounded or porous particles. Wet ball milling should ideally reduce size more efficiently than dry milling, but both methods can lead to particle agglomeration. If all methods still show 10 µm particle diameters, it suggests that either the starting material had large initial aggregates or that processing conditions were not optimized for finer size reduction.

Extraction of Cellulose from agricultural wastes:

Figure 11 show the FTIR spectra for the extracted cellulose after bleaching with acidified sodium chlorite. The absorption band at 897–1160 cm-1 associated with cellulose (19]. It can be seen that the purification of cellulose by acidified sodium chlorite treatment and alkaline treatment succeeded

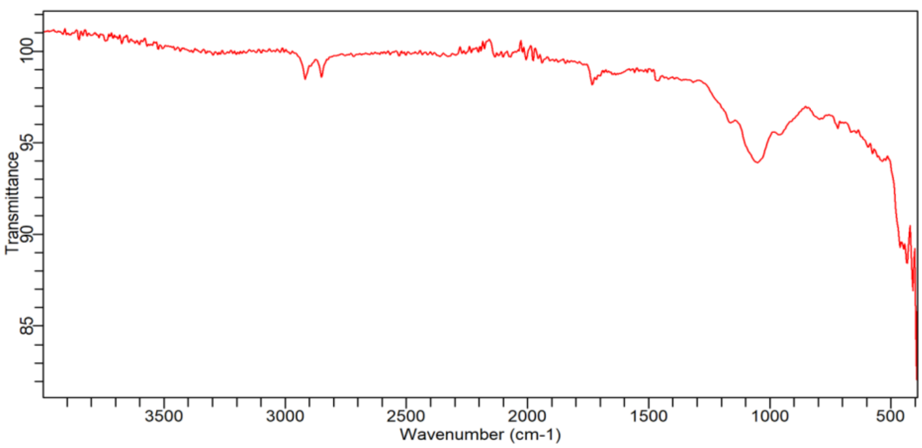

Figure 11. FTIR spectrum of extracted cellulose from the date palm tree.

Absorption band at 1429 cm^{-1} is assigned to the crystalline region while the absorption band at 893 cm^{-1} to the amorphous region [20]. Band at 708 cm^{-1} is for the relative amounts of Iβ crystal form. Hydroxyl (O-H) and C-H stretching vibrations are seen at 3329.98 and 2890.29 cm-1, respectively. A broad band centered at 1644 cm-1 is attributed to the OH bending mode of water. Band at 1025.94 cm-1 is assignable to coupling modes of C–O and C–C vibrations.

4. Conclusion:

In this project, We can convert bentonite clay into nanoparticles in several ways, and we succeeded in converting clay into nanobentonite, and we were able to extract cellulose from Date-Palm Tree residues by condenser. Conclusion of these experiments, it is clear to us that processing bentonite in four different ways to obtain nano bentonite showed us that increasing the grinding time with the poly milling device gives better results.

For extracting cellulose, the ammonium molybdate tetrahydrate did not give us a good bleaching, so that we performed the second bleaching with acidified sodium chlorite.

References:

1. Harvey, C. C., and G. Lagaly. 2013. "Bentonite - An Overview." In *Developments in Clay Science*. ScienceDirect.
2. Tahri, I., I. Ziegler Devin, J. Ruelle, C. Segovia, and N. Brosse. 2016. "Extraction and Characterization of Fibers from Palm Tree." *BioResources* 11 (3): 7016–7025.
3. Medvedeva, T. B., X. S. Cherepanova, V. N. Parmon, and N. V. Gromov. 2023. "Production of Cellulose Materials from Oat Agricultural Wastes: A Review of Recent Approaches." *Preprints* 2023120745. https://doi.org/10.20944/preprints202312.0745.v1.
4. Lonestar Minerals. "Calcium Bentonite Clay."
    - "Natural Sodium Bentonite Suppliers in China with Low Price - Sodium Bentonite and Bentonite."
    - "CP-150 Organophilic Clay | Modified Montmorillonite."
5. Murray, Haydn H. 2006. "Bentonite Applications." In *Developments in Clay Science*, vol. 2, 111–130. Elsevier. https://doi.org/10.1016/S1572-4352(06)02006-X.
6. Kutlic, A., G. Bedekovic, and I. Sobata. 2012. "Bentonite Processing." *Rudarsko-Geološko-Naftni Zbornik* 24: 61–65. https://www.scribd.com/document/377293209/Rudarsko-geološko-naftni-Zbornik-24-61-65-2012-Bentonite-Processing.
7. Li, Feng. "Uses of Bentonite." *Medium*. https://medium.com.
8. Abollino, O., et al. 2003. "Adsorption of Heavy Metals on Na-Montmorillonite: Effect of pH and Organic Substances." *Water Research*.
9. CMS Industries. "Bentonite Manufacturer, Supplier, and Exporter - Saudi Arabia." https://www.cmsindustries.in/bentonite-manufacturer-supplier-exporter-saudiarabia/.
10. El-Nagar, Doaa Ahmed, and Dalal Hereimas Sary. 2021. "Synthesis and Characterization of Nano Bentonite and Its Effect on Some Properties of Sandy Soils." *Soil and Tillage Research* 208: 104872. https://doi.org/10.1016/j.still.2020.104872.
11. Mahmoud, A. S. 2022. "Effect of Nano Bentonite on Direct Yellow 50 Dye Removal: Adsorption Isotherm, Kinetic Analysis, and Thermodynamic Behavior." *Progress in Reaction Kinetics and Mechanism* 47. https://doi.org/10.1177/14686783221090377.
12. Bukit, N. "Preparation of Natural Bentonite in Nano Particle Material as Filler Nanocomposite High Density Polyethylene (HDPE)." *PDF File*.
13. "A Review on Date Palm Tree Properties, Characterization, and Its Potential Applications." *ResearchGate*. https://www.researchgate.net/publication/337164611.
14. "Advancing Date Palm Cultivation in the Arabian Peninsula and Beyond: Addressing Stress Tolerance, Genetic Diversity, and Sustainable Practices." *ScienceDirect*.
15. El-Bana, Nour. "Palm Dates Tree Cultivation: Benefits and Agriculture Development - A Review Article." *ResearchGate*. https://www.researchgate.net/publication/355859502.
16. "Isolation and Characterization of Cellulose from Date Palm Tree Spathe Sheath." 2020. *Sustainable Chemistry and Pharmacy* 17: 100307. https://www.sciencedirect.com.
17. "Isolation and Characterization of Cellulose and α-Cellulose from Date Palm Biomass Waste." 2019. *ScienceDirect*.
18. Raza, Mohsin, Basim Abu-Jdayil, Fawzi Y. Banat, and Ali H. Al-Marzouqi. 2022. "Isolation and Characterization of Cellulose Nanocrystals from Date Palm Waste." *ACS Omega*.