Isolation and Characterization of Microcrystalline Cellulose and Preparation of Nano-Crystalline Cellulose from Tropical Water Hyacinth

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Abstract

Because of the conservation problems causes by the existence of water hyacinth (W.H) as an watery plant in water bodies of Iraq, our study aimed to make use of (W.H) by isolation of microcrystalline cellulose, and a new method of preparation of Nano crystalline cellulose. Microcrystalline cellulose was produced using base bleaching method by sodium hypochlorite [NaOCl] to remove unorganized region of cellulose and lignin to create particles comprising of micro crystal and preparing of Nano crystalline cellulose from microcrystalline cellulose by acid hydrolysis and ultrasonic treatment. The Nano crystalline and microcrystalline cellulose characterized by AFM, FTIR, XRD and TGA. FT-IR spectra of microcrystalline cellules and Nano crystalline cellulose show peaks at (1076.28, 1058.92) cm^{-1} and (1118.71, 1112.93) cm^{-1} refer to the stretching vibration of C–O and stretching vibration intermolecular ester bonding.

The AFM image shows that isolated microcrystalline cellulose have a diameter of (141.37 nm) and the prepared Nano crystalline have a diameter of (87.39 nm). The Thermo gravimetric analysis of cellulose showed a high decomposition temperature at (283°C) for microcrystalline cellulose and (253)°C for Nano crystalline cellulose .The thermal stability of microcrystalline cellulose was more than Nano crystalline cellulose XRD result possessed a segal crystallinity index of 92.8 % and a average crystal size of 41.7 A ° for Nano crystalline cellulose and a Segal Crystallinity Index of 86.4 % and a average crystal size of 55.3°A of microcrystalline cellulose.

Keywords: Isolation, water hyacinth, Nano-crystalline, cellulose, preparation.

Introduction

Water hyacinth is a natant plant kind that lives in water at fast reproducing prompted (W.H) has transformed into a weed in a (W.H) is known as the world's most noticeably awful amphibian weed because of its capacity to quickly cover entire conduits. The development of (W.H) inside a half year 125 tones wet weight in the range of 1 hectare few zones in Iraq water, for example, in numerous lakes or different bowls [1]. It frames thick, impervious tangles over the water surface, and other particular effects, for example blocking water system channels and streams, restricting livestock access to water, destroying natural wetlands, eliminating native aquatic plants, reducing infiltration of sunlight, changing the temperature, pH, oxygen levels of water , expanding water misfortune during transpiration (more prominent than dissipation from an untamed water body), modifying the natural surroundings of the oceanic life forms, confining recreational utilization of conduits, diminishing stylish estimations of conduits, decreasing water quality from deteriorating plant, devastating wall, streets and other framework when vast [2 & 3]. As a result of what originated from (W.H) it was necessary to control the spread of plant in nature. (W.H) is an incredible wellspring of biomass as bioenergy crude material. The Gasification of one-ton dry issue via air and steam at high temperatures (800 °C) gives roughly 1,100 m^3 natural gas (143 But/cuft) containing 52.8% N_2, 16.6% H_2, 4.8% methane, 21.7% CO and 4.1% CO_2. In addition, by, the high dampness substance of (W.H) causing high dealing with cost tends to restrict business wanders [4]. In customary process. (W.H) are utilized to make furniture, totes, rope, craftsmanship paper, bioethanol generation and fractional board [5]. High cellulose content in (W.H) (33% cellulose, 26% hemicellulose, and 9% lignin) can possibly be utilized as crude material for cellulose base polymer, which have a higher financial esteem compared to the present use. Cellulose is a natural polymer consisting of ringed glucose molecules. The repeat unit showed in figure (1) is comprised of two anhydroglucose rings $(C_6H_{10}O_5)n$, linked together through an oxygen covalently bonded to the C1 of one glucose ring and the C4 of the adjoining ring (1-4 linkage) and so called the β 1-4 glucosidic bond

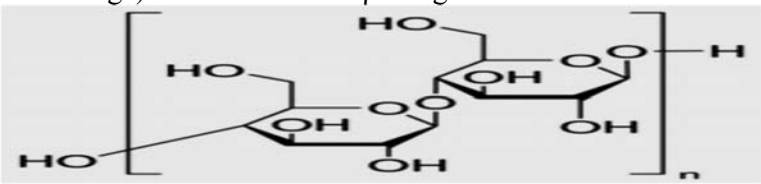


Figure (1): Molecular structure of a cellulose

In this study, microcrystalline cellulose has been isolated from (W.H). Microcrystalline cellulose was first presented in the mid-1960s. [6]. microcrystalline cellulose uses as a binder, fillers material and crushers, has smashed a moderately brief time, upgrade the stream properties of the granules [7]. The imported microcrystalline cellulose affects the cost expansion of medication available. Production of microcrystalline cellulose is commonly used in chemical methods by base hydrolysis process, utilizing a strong base and bleaching by sodium hypochlorite [NaOCl] to remove unorganized region of cellulose and make micro crystal particles. Nano crystalline cellulose can be extracted from natural resources such as sisal [8], flax, hemp and grass [9]. In addition, our study includes preparation of Nano crystalline cellulose from microcrystalline cellulose by acid hydrolysis and ultrasonic treatment. Nano scale cellulose particles have got increased much attention from both scholarly world and industry as another class of sustainable nanomaterial because of their valuable mechanical properties (High specific strength and rigidity and thermo stability) consolidated with their Nano scale crystalline and fibrous morphology, synthetic tunable surface functionalities, a capacity to be acquired in different dimension (esp. aspect ratio) and

inexhaustibility [10 & 11]. They have been investigated as fillers and rheology modifiers in different fields like foams [12], aerogels [13] and polymer electrolytes [14 &15]. Nano and microcrystalline cellulose were characterized by AFM, FTIR, and TGA.

Chemicals and Method

Chemicals

Water hyacinth in harsh fiber shape was gotten from the police channel in Baghdad, The stems were washed with water, dried, divided and pound. The grains were then sift utilizing 75 mesh and put away at 25C°. Benzene 95.9% (Sigma Aldrich), ethanol 99.8% (Sigma Aldrich), Sodium hypochlorite (Babylon company) , sodium hydroxide 97% (C.D.H), hydrochloric acid 37%(Sigma Aldrich) , sulfuric acid 98% (Romil).

Methods

Isolation of microcrystalline cellulose:

Water hyacinth powder were extracted by blended ethanol/ benzene solvent with proportion of 1:2 for (4 hr.) at 115°C.moreover bleaching process was done by 3% sodium hypochlorite [NaOCl] for (1 hr.) at 25°C. At that point, hemicellulose was removed by base hydrolysis with 17.5% (w/v) sodium hydroxide [NaOH] at 25°C for (2 hr.) The another bleaching was done to remove the rest of the lignin via cooking process was by 1% sodium hypochlorite [NaOCl] and stirred at 25°C for (1 hr.). The final stage was hydrolysis by 5% hydrochloric acid [HCl] as catalyst for (1 hr.) at 25°C. The solid sample washed with distilled water until free of acid

Preparation of Nano crystalline cellulose:

One gram of microcrystalline cellulose was added to 25 ml of 65% sulfuric acid [H_2SO_4] in round-bottom flask. The hydrolysis was done at 50°C with mixing for (1 hr.) the hydrolyzed product has handled with ultrasonic generator (Wise clean AO6H) with a steady energy of 100 W to enhance the acid hydrolysis. The product blend was centrifuged (TGL-16, Wei Jia Instrument Manufacturing Co., LTD., China) at 11,000 rpm for 10 min to isolate the Nano cellulose. In the meantime, the Nano cellulose was washed with distilled water and over and again centrifuged for five time. The suspension was collected and freeze-dried for testing.

Results and discussion

Fourier-transformed infrared spectra (FT-IR) analysis

Figure (2) demonstrates the FT-IR (830 Shimadza Spectrophotometer) spectra of microcrystalline cellules and Nano crystalline cellulose, individually. In general, microcrystalline and Nano crystalline cellulose samples, showed a strong band at (3433.29, 3417.86) cm^{-1}, which belong to stretching vibration of O-H group [16]. The characteristic peak at (2915,2900.94) cm^{-1} was because of the symmetric C– H vibrations [17,18]. Thus, strong adsorption at (1639.49 cm^{-1}) was belong to adsorbed water a cellulose surface. Moreover, the peaks at (1076.28, 1058.92) cm^{-1} , (898.83, 896.90) cm^{-1} and (1118.71, 1112.93) cm^{-1} referred to the stretching vibration of C–O [19], C-OH out of plane bending mode [20 & 21] and stretching vibration intermolecular ester bonding.

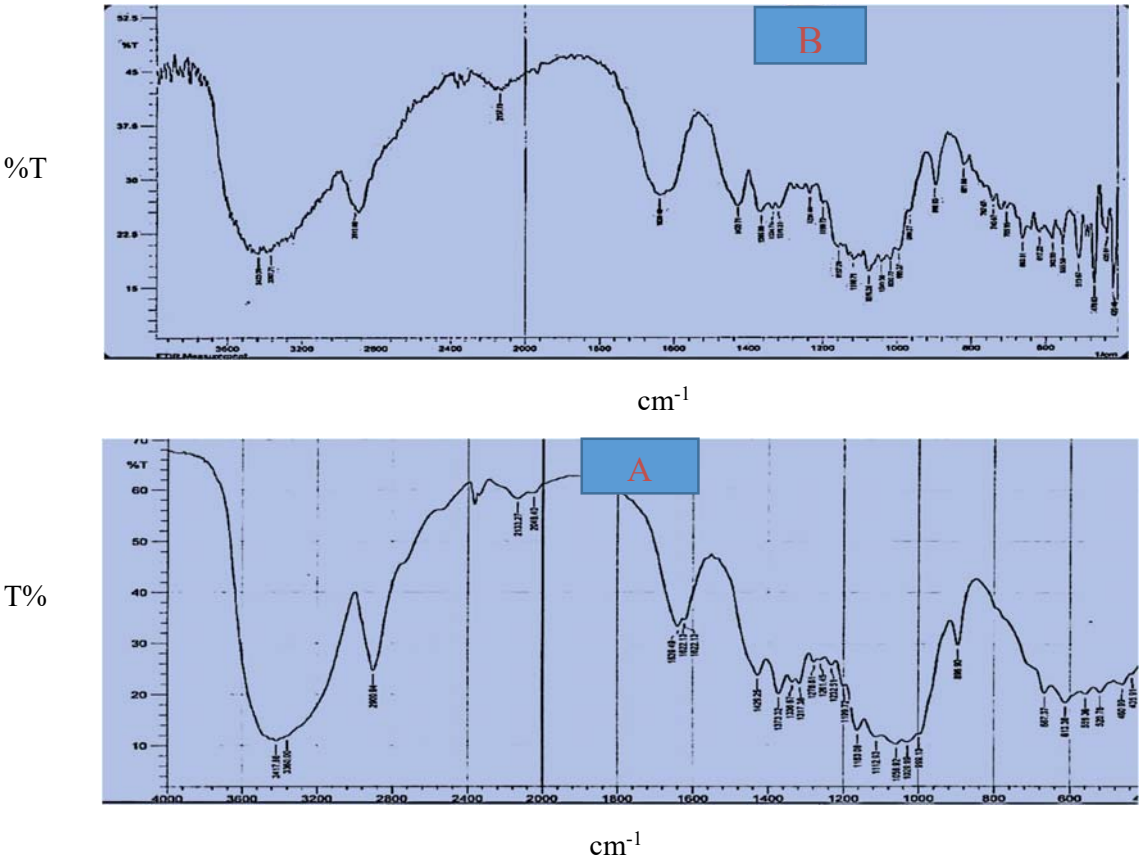


Figure (2): (B) FT-IR spectra of microcrystalline cellulose, (A) FTIR spectra of Nano crystalline cellulose

Characterization and Morphology:

Cellulose samples are Atomic Force Microscope (AFM) Angstrom Advanced Inc. USA AA (300 Scanning probe microscope) images of the microcrystalline and Nano crystalline shown in Figure (3). It can be seen that microcrystalline cellulose particles display curled and well-defined shape fibrils. The calculated average particle sizes of microcrystalline cellulose were (141.37 nm) and this size in the range micro scale. After sulfuric acid hydrolysis and ultrasonic treatment, the microcrystalline cellulose was converted into Nano-sized cellulose Figure (4). The calculated average particle sizes of Nano crystalline cellulose were as (87.39 nm) and this size in the range Nano scale These results are according to previous studies [22].

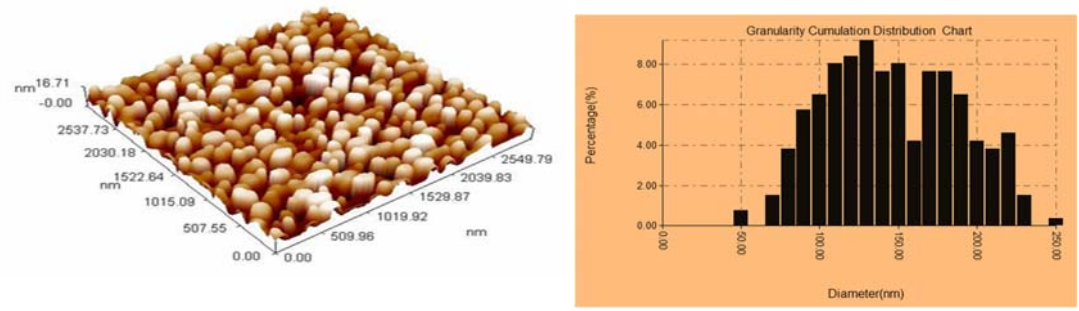


Figure (3) : AFM images and diameter allocation of microcrystalline cellulose

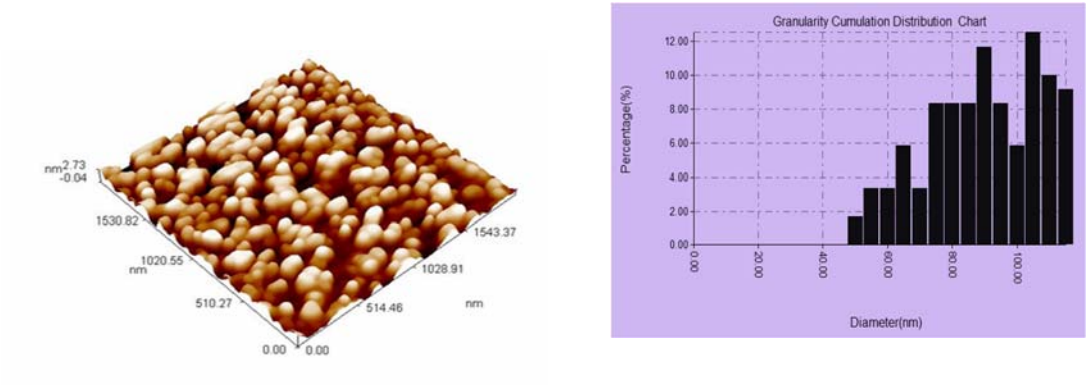
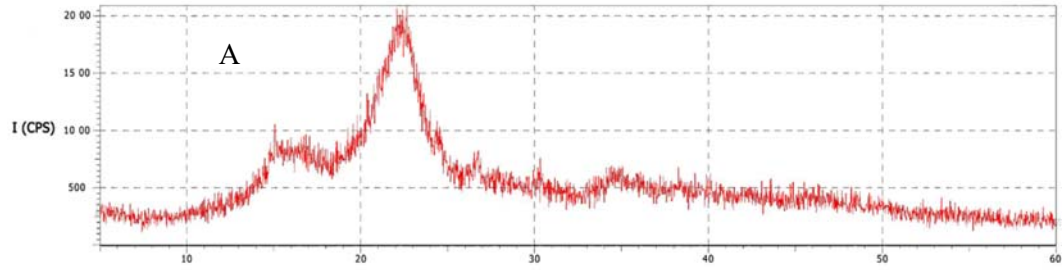


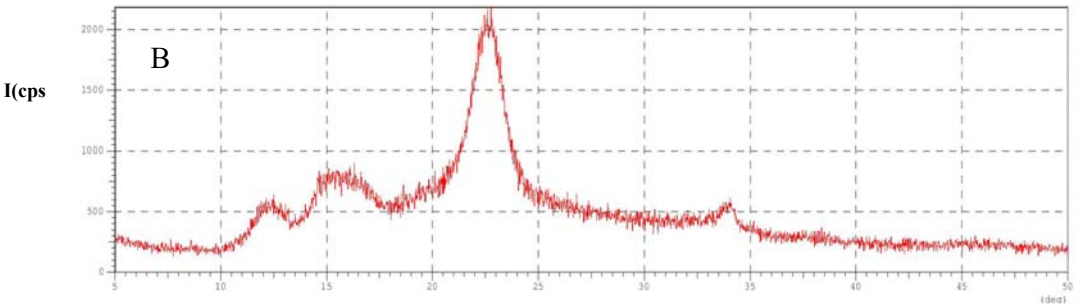
Figure (4): AFM images and diameter allocation of Nano crystalline cellulose.

X-ray diffraction

X-ray diffraction patterns for microcrystalline cellulose and Nano crystalline cellulose samples were performed on a diffractometer (Shimadzu 600) with Cu Kα radiation (k = 0.154 nm) at 40 kV and 30 mA. XRD data were collected from 2θ = 10°–60° at a scan rate of (0.02deg) XRDs of microcrystalline cellulose and Nano crystalline cellulose are demonstrated in Figure (5), respective. The characteristic diffraction peaks at 2θ angles of around 14.9°, 16.5°, 20.8°, 22.6°, and 34.5° assigned to the typical reflection planes of cellulose 110 $1\bar{1}0$, 012, 200, and 004, respectively, were preserved [23]. The crystallinity indices (Xc) of CNs were calculated according to the Segal method (eqn (2)) [24], which exhibited a high crystallinity (about 86.4% for microcrystalline cellulose and about 92.8% for Nano crystalline cellulose) and maintenance of the crystalline structure. From the calculation according to the Scherrer equation (eqn (3)) [25], the average sizes of 200, 110, and $1\bar{1}0$ planes of cellulose Nano crystalline were about (41.7A°) and microcrystalline (55.3A°) these results are according to previous studies [26]



2 Theta (deg)

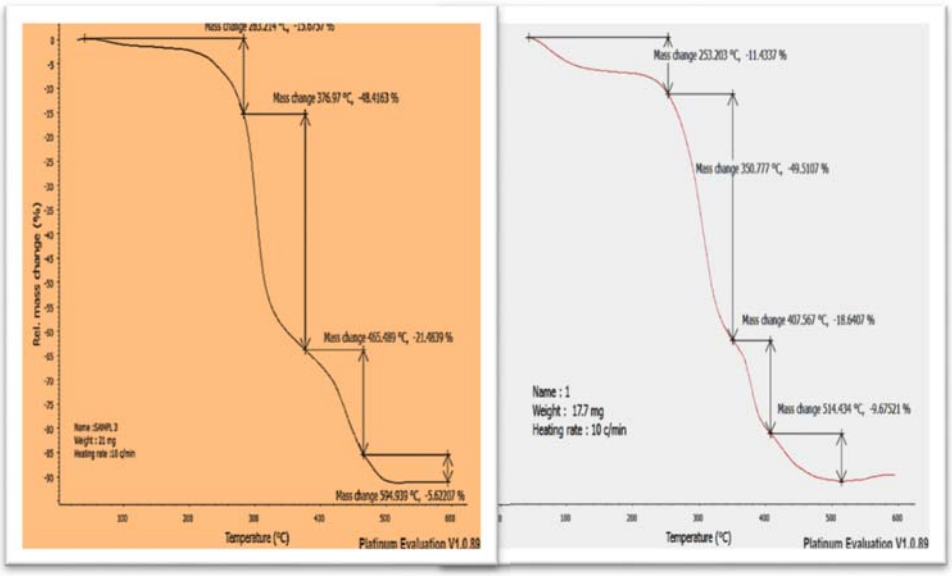


2 Theta (deg)

Finger (5): (A) X-ray diffraction patterns for microcrystalline cellulose
B) X-ray diffraction patterns for Nano crystalline cellulose

Thermo gravimetric analysis (TGA)

Figure (6) demonstrates the thermal behaviors microcrystalline cellulose, and Nano crystalline cellulose. The initial little weight reduction (nearly 5% at a less than 100°C) refers to the evaporation of absorbed water. For microcrystalline cellulose there was a small weight reduction up to (282.214 °C), and an intense loss at (376.97°C), followed by slow weight loss up to (407.567°C). For Nano crystalline the large most of weight reduction happened in the scale of (350.777 °C). In addition, the huge weight reduction began at around (253.203°C) and finished at (407.567°C). These results are according to previous studies [27 & 28].



(A) (B)

Figure (6): (A) TG-curves for microcrystalline cellulose, (B) TG-curves for Nano crystalline cellulose

Conclusion

Microcrystalline cellulose was isolation from the watery weed (W.H) by chemical process and production of Nano crystalline cellulose by chemical and mechanical medications. The AFM examination shows that the pure microcrystalline cellulose has been acquired after the chemical treatment and evaluated the separated Nano crystalline cellulose are having diameter of 87.39nm. The FTIR spectra affirmed the evacuation of hemicelluloses and lignin when treated with sodium hypochlorite and sodium hydroxide consequently at different time interim at suitable temperatures. The TGA analysis indicated that the micro and Nano crystalline cellulose were pure due to low decomposition temperature of hemicelluloses and lignin (under 200°C). Our study has highlighted the utility of the aquatic weed, which is considered as a main reason for impure in numerous region. It has additionally show the feasibility of production Nano crystalline cellulose, which have a powerful application in the near future. Additionally, studies will indicate the uses of this Nano and microcrystalline cellulose.

References

[1] Hu; Zhifeng; Xiaoqian Ma; and Longjun. "Optimal conditions for the catalytic and non-catalytic pyrolysis of water hyacinth." Energy Conversion and Management 94, 337-344, 2015
[2] Istirokhatun; Titik. "Cellulose isolation from tropical water hyacinth for membrane preparation." Procedia Environmental Sciences 23, 274-281, 2015.
[3] Guna; Vijay Kumar. "Water Hyacinth: A Unique Source for Sustainable Materials and Products." ACS Sustainable Chemistry & Engineering 2017.
[4] J. Duke. "Handbook of Energy Crops. Available at: http." newcrop. hort. purdue. edu/newcrop/duke_energy 1983.
[5] Istirokhatun; Titik. "Polymeric Membrane Made of Cellulose Isolated from Tropical Water Hyacinth Blended with Chitosan." IOP Conference Series: Earth and Environmental Science. 55.. 1. IOP Publishing, 2017.
[6] A. Nitin; Bhimte; and T. Pralhad. "Evaluation of microcrystalline cellulose prepared from sisal fibers as a tablet excipient: a technical note." Aaps Pharmscitech 8.1, E56-E62, 2007.
[7] R. Rowe; S. Paul; and E. Q. Marian. "Handbook of Pharmeceutical Exicipient 6th." 2009.
[8] Siqueira; Gilberto. "Morphological investigation of nanoparticles obtained from combined mechanical shearing, and enzymatic and acid hydrolysis of sisal fibers." Cellulose 17.6, 1147-1158, 2010.
[9] Amiralian; Nasim. "Easily deconstructed, high aspect ratio cellulose nanofibres from Triodia pungens; an abundant grass of Australia's arid zone." RSC Advances 5.41, 32124-32132, 2015.
[10] J. Robert; Moon. "Cellulose nanomaterials review: structure, properties and nanocomposites." Chemical Society Reviews 40.7,3941-3994, 2011.
[11] J. Stephen.; Eichhorn. "current international research into cellulose nanofibres and nanocomposites." Journal of materials science 45.1, 1, 2010.
[12] Mendez; Julie. "Bioinspired mechanically adaptive polymer nanocomposites with water-activated shape-memory effect." Macromolecules 44.17, 6827-6835, 2011.
[13] Ben Azouz; Kaouther. "Simple method for the melt extrusion of a cellulose nanocrystal reinforced hydrophobic polymer." ACS Macro Letters 1.1, 236-240, 2011.
[14] Svagan; J. Anna.; A. Lars. Berglund; and Poul Jensen. "Cellulose Nanocomposite Biopolymer Foam Hierarchical Structure Effects on Energy Absorption." ACS applied materials & interfaces 3.5,1411-1417, 2011
[15] Hayase; Gen. "Polymethylsilsesquioxane–cellulose nanofiber biocomposite aerogels with high thermal insulation, bendability, and superhydrophobicity." ACS applied materials & interfaces 6.12, 9466-9471, 2014.
[16] Azizi Samir; My Ahmed Said. "Nanocomposite polymer electrolytes based on poly (oxyethylene) and cellulose nanocrystals." The Journal of Physical Chemistry B 108.30, 10845-10852, 2004.
[17] Cranston; D. Emily; and G. Derek. Gray. "Morphological and optical characterization of polyelectrolyte multilayers incorporating nanocrystalline cellulose." Biomacromolecules 7.9, 2522-2530, 2006
[18] Yang; Qiang. "Synthesis and characterization of cellulose fibers grafted with hyperbranched poly (3-methyl-3-oxetanemethanol)." Cellulose 18.6, 1611-1621, 2011.
[19] M .Jahan; Sarwar. "Jute as raw material for the preparation of microcrystalline cellulose." Cellulose 18.2, 451-459, 2011.
[20] Zaman; Masuduz. "Synthesis and characterization of cationically modified nanocrystalline cellulose." Carbohydrate Polymers 89.1, 163-170, 2012.
[21] X. Sun. "Characteristics of degraded cellulose obtained from steam-exploded wheat straw." Carbohydrate research 340.1, 97-106, 2005.

[22] Morán; I. Juan. "Extraction of cellulose and preparation of nanocellulose from sisal fibers." Cellulose 15.1, 149-159, 2008.
[23] Lin; Ning; Cécile Bruzzese; and Alain Dufresne. "TEMPO-oxidized nanocellulose participating as crosslinking aid for alginate-based sponges." ACS applied materials & interfaces 4.9, 4948-4959, 2012.
[24] Terinte; Nicoleta; Roger Ibbett, and Kurt Christian Schuster. "Overview on native cellulose and microcrystalline cellulose I structure studied by X-ray diffraction (WAXD): Comparison between measurement techniques." Lenzinger Berichte 89, 118-131, 2011.
[25] French; D. Alfred. "Idealized powder diffraction patterns for cellulose polymorphs." Cellulose 21.2, 885-896, 2014.
[26] Tang; Yangon; et al. "Preparation and characterization of nanocrystalline cellulose via low-intensity ultrasonic-assisted sulfuric acid hydrolysis." Cellulose 21.1, 335-346, 2014.
[27] Cha; Ruitao; Zhibin He; and Yonghao Ni. "Preparation and characterization of thermal/pH-sensitive hydrogel from carboxylated nanocrystalline cellulose." Carbohydrate Polymers 88.2, 713-718, 2012.
[28] Wang; Neng; Enyong Ding; and Rongshi Cheng. "Thermal degradation behaviors of spherical cellulose nanocrystals with sulfate groups." Polymer 48.12, 3486-3493, 2007.
[29] O. Ishida. "Microfibrillar carbon from native cellulose." Cellulose 11.3, 475-480, (2004).
[30] Morán; I. Juan. "Extraction of cellulose and preparation of nanocellulose from sisal fibers." Cellulose 15.1, 149-159, 2008.