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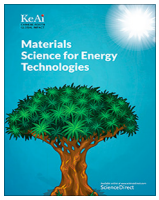

Process optimization for the production of cellulose nanocrystals from rice straw derived α-cellulose

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ABSTRACT

Nanocrystalline cellulose has emerged out as a substantial nanomaterial in recent years due to its peculiar characteristics such as bio renewability and sustainability while having high mechanical strengths, optical transparency and much more. In this study, we prepared cellulose nanocrystals (CNC) by acid hydrolysis of rice straw derived cellulose. The aim was to maximize the product yield by using RSM (response surface methodology) and also to investigate the interaction between 3 design factors; concentration of acid, temperature of reaction and time period of the reaction to unriddle their effects on yield of the product. A high CNC yield of 90.28% was found when the reactions conditions were kept at temperature 30 °C, acid concentration 75 wt% and time 5 h. Morphological characterization through scanning electron microscopy (SEM) clearly showed the formation of rod shaped CNCs. X-ray diffraction (XRD) and thermogravimetric analysis (TGA) revealed that CNC's have higher crystallinity (76%) than that of rice straw derived α-cellulose and higher thermal stability respectively. Thus, the isolated CNC may be suitable for use as reinforcing agent in the fabrication of bio-nanocomposites for different applications.

1. Introduction

Rice is one of the largely cultivated grain crop across worldwide. It is usually planted in the month of May and harvested during the mid-October. The production of rice straws as a harvest residue of rice crop, accounts for 45% of the total volume. With the annual production capacity of 667.6 million tons of rice straw, Asia is the largest producer followed by Africa (20.9 million tons) and Europe (3.9 million tons) respectively [1].

The rice straw is usually of less importance because of negligible nutrient source and when combusted as a fuel source, produces large amount of ash and other hazardous content directly in the atmosphere. The major composition of rice straw includes cellulose (38.3%), hemicellulose (31.6%), lignin (11.8%), and silica (18.3%). Rice straw from certain varieties of rice could be used for animal feed stock and other can be used in papermaking industry. However, the total amount of valuable products formed is very low. Hence, this urge for the proper management for the disposal of rice straw from ecological point of view [2–3].

Though rice and wheat cropping system is one of the major cropping systems in India and these crops cover almost 35–40 lakh hectares of area in Punjab. 14 million tons of straw is produced with the cultivation of rice which further escalates to 20 million in case of wheat. The wheat straw can be used as a fooder for cattle but the poor management of the rice straw has always remained the alarming problem as merely burning of the rice straw gives birth to more serious issues like environment pollution, health problems, road accidents etc.

The production of rice straw is about 220 lakh tonnes that result primarily from paddy fields every year, out of which of 90 per cent of them are burnt in the field itself. The reason for this is the general misconception among the farmers the time period between sowing of wheat and harvesting of rice is very short which is not enough for decomposition of rice straw. So, many of the farmers adopt the easiest way to manage the rice residue by burning it in the field resulting in the side effects in the environment.

There are several effects of burning of rice straw. For instance, burning of rice straw leads to the destruction of many important soil nutrients; 400 kg of carbon, 5.5 kg of nitrogen, 2.3 kg of phosphorus and 1.2 kg of sulphur are lost as a result of burning of 1 tonnes of rice straw. Moreover, due to the heat accumulated by burning of paddy straw there gets scarcity of microbes in the

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soil. Thus, straw burning adversely affects the soil health and soil fertility. Another major issue is the burning results in the emission of many gases such as carbon dioxide (70%), methane (0.66%), carbon monoxide (7%), nitrous oxide (2.09%) and ash which cause the environment pollution and change in climate. This results in the adverse effects on health of humans as well as of animals. Smoke screen which comes at the burning of rice straw leads to the transportation problems and road accidents which ultimately cause destruction to invaluable live and wealth. Biodiversity also gets affected as the road side's plant and trees also catches fire in the process of burning straw.

Cellulose is one of the most significant natural polymers on Earth and a main source of sustainable products appropriate for industrial applications. In physical appearance, cellulose is a fibrous, hard, water-insoluble substance that plays an important part in keeping the composition of plant cell walls. And chemically, it comprises of a linear homopolymer of b-D-glucopyranose units connected by glycosidic bond, with a repeating subunit consisting of two connected glucose units. Nanomaterials which are derived from cellulose are sustainable as well as renewable. There is a great diversion of interest towards nanocellulose to be used as filler in various nanocomposites which have a great potential for industrial as well as biomedical field. Nanocellulose shows excellent properties like low density, high tensile strength, low toxicity and high aspect ratio [4]. The most fascinating properties of nanocellulose are the presence of -OH (hydroxyl group) which can be functionalised easily. As a result of vigorous study on these properties, nanocellulose is being used in various applications like it is being used as nanofiller in polymer composites, protective coatings, membrane of filtration system, antimicrobial films and substrate for electronical items and batteries. [5–6]. Cellulose nanomaterials which are derived from different sources like plants, animals etc fall in two categories namely cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) [7–8]. Cellulose nanocrystals can either occur as cellulose Nano whiskers (CNW) or nanocrystalline cellulose (NCC) [9–10]. Nano fibrillated cellulose (NFC) or micro fibrillated cellulose (MFC) are the names given to cellulose nanofibrils (CNFs) depending on the size and method of extraction [11–12,13]. CNCs are needle-like cellulose particles with a highly crystalline nature that has at least one dimension equal to or less than 100 nm [14–16].

Intensive research has been done in details in a couple of decades on the production of nanocellulose from different natural sources like wheat straw [17], sugarcane bagasse [18 19], cotton [20 21] etc. But the rice straw which is abundantly available worldwide and renewable too has not been exploited well for its use for the production of nanocellulose in accordance to its usage as a reinforcing agent in different bio composites. In prior research, few methods have been indicated to extract CNCs from rice straw as agro-waste, such as elevated pressure homogenization [22], acid-hydrolysis [23–26] alkaline hydrolysis followed by acid-hydrolysis, but comprehensive research is required to extract and characterize CNCs from these waste materials and use them for value-added products.

Response surface methodology was developed by G. E. P. Box and K. B. Wilson in 1951. The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response. Box and Wilson suggest using a second-degree polynomial model to do this. They recognize that this model is only an approximation, but they use it because it is simple to predict and apply such a model, even if little is known about the method. This word was invented from the mathematical model's graphical perspective produced after fitness. RSM comprises of a set of empirical model building mathematical and statistical techniques [27–28].

The primary objective of this research is to optimize process circumstances using the technique of sulphuric acid hydrolysis to separate nanocrystals of cellulose with greater yield and better index of crystallinity. As mentioned previously, cellulose acid hydrolysis is a well-known method for the manufacturing of cellulose nanocrystals, but manufacturing is often restricted to quantities that are only adequate for use on a lab scale. As for the use of CNC to make various polymer composites, there is a need for greater quantities of nanocellulose. This requires process parameter optimization resulting in greater output and a better index of crystallinity.

In this work, we developed an optimized CNC preparation protocol using central composite design and chosen three variables to explore hydrolysis of α-cellulose; initial conc. of H_2SO_4, the reaction time and the temperature at which the response took place. The CNCs obtained were characterized for surface topography and morphology by FE-SEM, AFM, and TEM, chemical and physical and elemental characterization by FTIR spectroscopy, XRD, EDX and thermal properties by thermo-gravimetric analysis (TG, DTG, and DTA). Image analysis of the extracted product was also done using Image J software to investigate the length and diameter of the CNCs. The research for large-scale production of nanocrystal using rice straw waste will be worthwhile in this respect.

2. Materials and methods

2.1. Materials

Rice straw was collected from the local farms of Mohali, Punjab, India. Rice straw was first cleaned and then dried to remove any impurities or dust. It was then ground using commercial grinder (PX-MFC 90). All chemicals like Sodium hydroxide flakes (NaOH, CDH-97%), sodium chlorite ($NaClO_2$), 80%, technical grade, Sigma Aldrich), acetic acid glacial (100%, Emparta grade, Merck) and sulphuric acid (H_2SO_4, 98%, Emparta grade, Merck) were used as without further purification.

2.2. Preparation of cellulose from rice straw

Process parameters which were used in the preparation of α-cellulose from rice straw have been already optimized in our previous work [29]. Preparation of cellulose from a biomass is a two-step process – namely pre-treatment and delignification. The rice straw were first soaked in hot water and kept under stirring for 1 h to remove wax and other substances, then left for overnight drying in hot air oven at 40 °C. The dried rice straw was then grounded into fine rice straw powder (1 g/10 ml) and was treated with 12 wt% NaOH at 121 °C for 1 h. It was done to remove lignin and hemicelluloses from rice straw and to purify the cellulose. The solution acquired was then centrifuged, washed with water continuously until the solution's pH became neutral. The pre-treated neutral residue was then oven-dried overnight at 50 °C. The pre-treated residue obtained was treated with 5 wt% acidified sodium chlorite at 75 °C for 90 min. pH was in the range of 3–5 (adjusted with 1 M glacial acetic acid). At the end of the reaction, delignified residue known as α cellulose was obtained and washed with distilled water until the pH became neutral and them was dried in oven overnight at 50 °C [3].

2.3. Preparation of cellulose nanocrystals

The α-cellulose obtained was treated with different concentrations of H_2SO_4 (45–75 wt%), at different temperature range (30 °C–50 °C) for different hydrolysis time periods (1–3 h). The

bath ratio of the solid cellulose to liquor was 1:20 (%wt). The hydrolysed cellulose sample was washed several times with distilled water by centrifugation (10,000 rpm & 15 min) in order to remove the excess of sulphuric acid. The suspension was then dialyzed against distilled water until a constant pH was reached and finally the resulting suspension was sonicated using probe sonicator (SonicsVibra cell) to correctly disperse suspended nanocrystals and then freeze dried. The net yield of CNCs was calculated as the ratio between the weights of the freeze dried hydrolysed residue and initial weight of cellulose. Finally at optimized condition, the α cellulose content was also analyzed by standard procedure of TAPPI T 203 cm-99.

2.4. Characterization methods

2.4.1. FTIR-ATR

The FTIR-ATR sample spectra were recorded on an instrument (Agillent Technologies Carry 600) with a resolution of 4 cm^{-1} in the range of 400–4500 cm^{-1} before and after treatment.

2.4.2. Thermogravimetric analysis

The thermogravimetric analysis of the crystals was performed at a temperature interval of 25 °C–800 °C at a heating pace of 10 °C per minute under the nitrogen atmosphere. For the research, the heat analyser Mettler Toledo was used.

2.4.3. Scanning electron microscopy

A benchtop scanning electron microscope (JEOL JCM 6000 Nikon Corporation) was used to examine surface morphological distinctions at an acceleration voltage of 10.0 kV. Before scanning, a intelligent coater (25 mm stub size) covered the crystals with gold.

2.4.4. X-ray diffraction

High crystallinity was obtained using X-Ray diffractometer (XPERT-PRO D8 Bruker) fitted with Cu Kα (α = 0.154 nm) in the second range 5–400, (battery energy settings: 40 kV and 40 mA). The empirical method was used to obtain the crystallinity index, X_c of samples as shown in Eq. (1) [24]

$$Xc = \frac{I_{002} - I_{am}}{I_{002}} X100 \quad (1)$$

where I_{002} and I_{am} are the peak intensities of crystalline and amorphous materials, respectively.

Scherrer Eq. (2) is used to calculate the crystalline size

$$\tau = \frac{\kappa\lambda}{\beta\cos\theta} \quad (2)$$

where,

τ is the crystal dimension perpendicular to the diffracting planes with Miller Indices of hkl
λ is the wavelength of the X-ray radiation (λ = 0.154 Å)
β is the full width at half maximum (FWHM) of the diffraction peaks [25].

2.4.5. High resolution transition electron microscopy (HR-TEM)

Cellulose Nanocrystals and Nano crystal bundles were gathered at an accelerating voltage of 120 kV using the FEI Tecnai F20. Drops of diluted cellulose Nano crystal suspensions (1 ml, 0.01 wt%) were placed on glow-discharged, carbon-coated electron microscopy grids for 5 min in a water bath sonicator and negatively stained. The excess liquid was removed by a piece of filter paper followed by drying at room temperature.

2.5. Optimization of parameters for acid hydrolysis

RSM is a statistical instrument for experiment design, empirical model building, and factors impact assessment. RSM can decrease the amount of experimental tests required to assess various parameters and their interactions. The STATISTICA software (StatSoft, USA, version 10) used the design and evaluation of the tests.

In view of the results of the earlier work reported on CNC, the following three factors were examined through a central composite design: the concentration of sulphuric acid, temperature and time of reaction. Each factor varied at three levels: concentration of sulphuric acid (wt %) 45–75, Time (h) 1–5, Temperature 30–50 (°C). The response was the yield of CNC with respect to the initial weight of cellulose. Design led to a total of 20 experiments (Table 2). Using the reaction surface model and the point prediction of design specialist software, the expected ideal values of the variables were recognized. At ideal circumstances, validation studies were conducted in triplicate. The measured reaction was given with the predicted response to validate the appropriate values.

3. Results and discussion

3.1. Optimization of parameters

Methodology of the response surface using central composite design was used to determine the optimum concentrations of the three chosen variables affecting the yield of CNCs. The relevant factors were sulphuric acid concentration, temperature and reaction time. Each factor has been tested on three levels. Through the one-at a time variation of variables, the center point concentrations were held at ideal values.

The response surface model was as follows:

$$\text{Yield}\ (\%) = 65.82 + 4.00A + 4.20B - 11.8C + 14.14A^2 + 17.14B^2 - 22.86C^2 - - 12.25AB + 8.75AC - 22.75BC \quad (3)$$

where, A is the acid concentration in wt%, B is the time in hours and C is the Temperature (°C) of the reaction (Table 1).

The maximum yield of 90% was measured in run 20 with the predicted value of 83%. The ANOVA of the response surface model (Eq. (3)) is shown in Table 2. The F-value for the model (i.e. Eq. (1)) was 3.31 (Table 3), which implies that the model is significant and there is only 3.92% of the chance that this value of F could occur due to the experimental noise (Table 3). The temperature of the reaction, concentration of sulphuric acid and time taken for the reaction has a significant effect on the response as indicated by the value of P which is less than 0.05 (Table 3). The R^2 value indicates the degree to which the model was able to predict the response. The determination coefficient (R^2) of the model (Eq. (3)) was 0.9612. In the case when P value is smaller than 0.05, the parameters are considerably varied and the analysis result is statistically significant value [30]. In this case, the data from predicted and observed values (Table 2) also showed that the model was significant with high degree of correlation coefficient (Fig. 1).

Contour plots also used the reaction surface model to predict the outcome. Contour plot is a two-dimensional plane projection

Table 1
Ranges of the factors used in central composite design for acid hydrolysis of cellulose.

Factors	Actual levels of coded factors		
	−1 (Low)	0 (Center)	+1 (High)
Concentration of acid (wt%)	45	60	75
Time (h)	1	3	5
Temperature (°C)	30	40	50

Table 2
Experimental setup and results for the central design matrix for acid hydrolysis of cellulose.

Trial No.	Concentration (wt%)	Time (mins)	Temperature (°C)	Yield (%) Predicted	Yield (%) Experimental
1	60	3	30	65.90	75
2	60	3	40	60.00	57
3	45	1	50	74.28	56
4	45	5	50	55.72	61
5	60	1	40	68.80	79
6	75	1	50	74.28	92
7	75	3	40	60.00	80
8	60	3	40	60.00	58
9	60	3	40	60.00	41
10	60	5	40	73.00	81
11	45	5	30	90.28	89
12	60	3	40	60.00	60
13	45	3	40	60.00	77
14	45	1	30	63.32	60
15	75	5	50	55.72	51
16	60	3	40	60.00	55
17	60	3	40	60.00	52
18	75	1	30	63.32	57
19	60	3	50	54.10	45
20	75	5	30	90.28	83

Table 3
ANOVA for Reduced Quadratic model.

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model				3.31	0.0392	Significant
(1) Acid conc. (wt%) (L)	40.000	1	40.000	17.1429	0.053680	
Acid conc. (wt%) (Q)	133.938	1	133.938	57.4019	0.016979	
(2) Time (mins) (L)	44.100	1	44.100	18.9000	0.049050	
Time (mins) (Q)	196.796	1	196.796	84.3413	0.011650	
(3) Temperature (°C) (L)	348.100	1	348.100	149.1857	0.006636	
Temperature (°C) (Q)	350.004	1	350.004	150.0017	0.006601	
1L by 2L	300.125	1	300.125	128.6250	0.007685	
1L by 3L	153.125	1	153.125	65.6250	0.014898	
2L by 3L	1035.125	1	1035.125	443.6250	0.002247	
Lack of Fit	814.575	5	162.915	69.8207	0.064180	Not significant
Pure Error	4.667	2	2.333			
Total SS	3285.529	16				

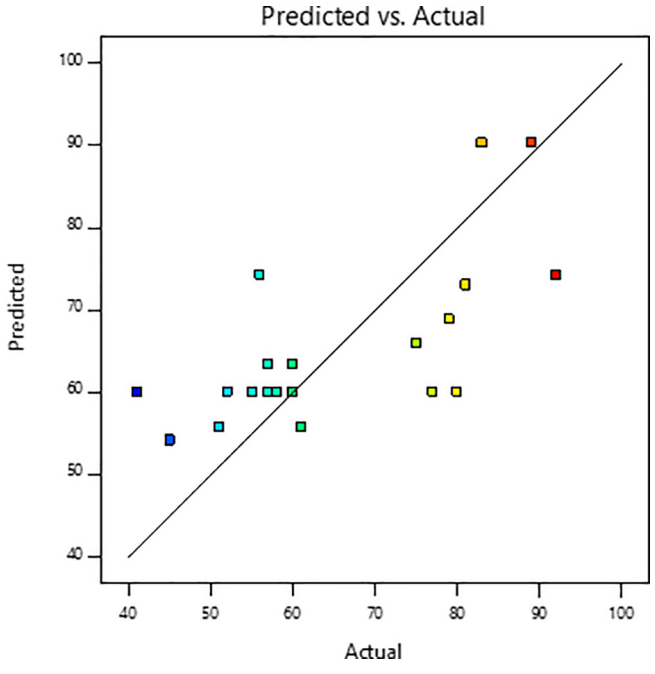

Fig. 1. Predicted vs. Actual graph.

of the reaction surface [31]. The contour plot forms show the nature and magnitude of the interaction between distinct variables. The circular nature of the contour plots indicates less prominent or negligible interactions, whereas the elliptical nature of the contour plots otherwise indicates comparatively prominent interactions.

The response surface plots were represented in Fig. 2, which showed the impacts on the reaction of the pair-wise mixture of the three variables. One factor was held at their center point level when producing these plots. Fig. 2 plots provide a visual indication of how the reaction was interactively influenced by any two variables. Fig. 2A presented the impact of variable sulphuric acid concentration and reaction time with temperature maintained at a steady temperature of 75 °C. Fig. 2B presented the impact of variable sulphuric acid concentration and reaction temperature with time maintained constant at 3 h, while Fig. 2C showed the impact of time and temperature at a steady acid concentration of 60 wt%. Overall, it can be shown that all three variables have important effects such as temperature, concentration and time. The central points of the contour plots were used to identify the optimized conditions. The validation experiments were carried out at optimized condition which was at acid concentration 75 wt%, reaction temperature 30 °C and reaction time of 5 h which gives average 90% yield of CNC, which was calculated according initial weight of α cellulose taken when run in triplicate. The α-cellulose content of raw biomass (rice straw) and the product CNC were found out to

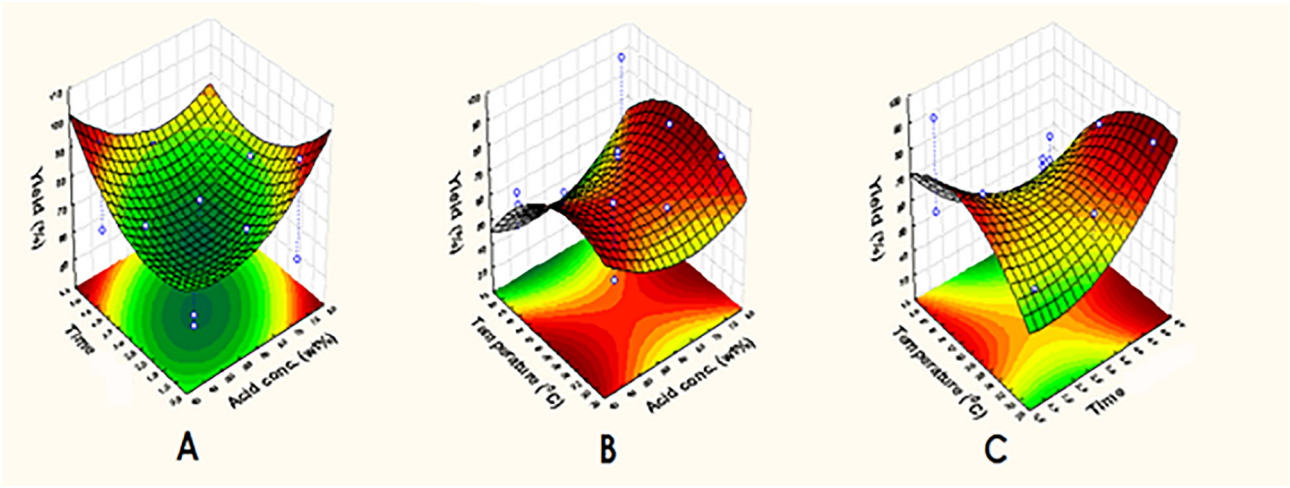

Fig. 2. . (A) Contour plot between conc. of H_2SO_4 (%) and Time (h); (B) Contour plot between conc. Of H_2SO_4 (%) and Temperature (°C); (C) Contour plot between Temperature (°C) and Time (h).

be 46.5% and 89.2% respectively, so if net yield of cellulose to be considered in the CNC, it will be 91.8%, which is significant enough according to α cellulose extracted from rice straw.

3.2. Characterization methods

3.2.1. Scanning electron microscopy

Electron microscopy scanning is a method to obtain high-resolution surface pictures. It includes scanning over a sample a fine beam of electrons and detecting the emitted signals. Imaging must be performed under vacuum in the SEM, since electrons cannot move through air. As shown in SEM micrographs (Fig. 3) it can be clearly depicted that after acid hydrolysis of cellulose, cellulose has been broken into various small rod like crystals.

3.2.2. FTIR-ATR

Cellulose and CNC show similar FTIR spectra (Fig. 4) which indicates that there are not any new formation of bonds during acid hydrolysis of cellulose. The spectral band of cellulose and CNC around 3400 cm^{-1} corresponds to the O–H bending, 2400 cm^{-1} is due to C–H group, 1060 C–O signifies the C–O bending of pure cellulose. The spectral bands around 897 cm^{-1} are associated with the cellulosic β-glycosidic linkages. Peak around 1054 cm^{-1} is due to C–O–C pyranose ring, peak at 902 cm^{-1} is associated with the glycosidic linkages between glucose units in cellulose II structure.

Fig. 3. SEM image of cellulose (rod like crystals).

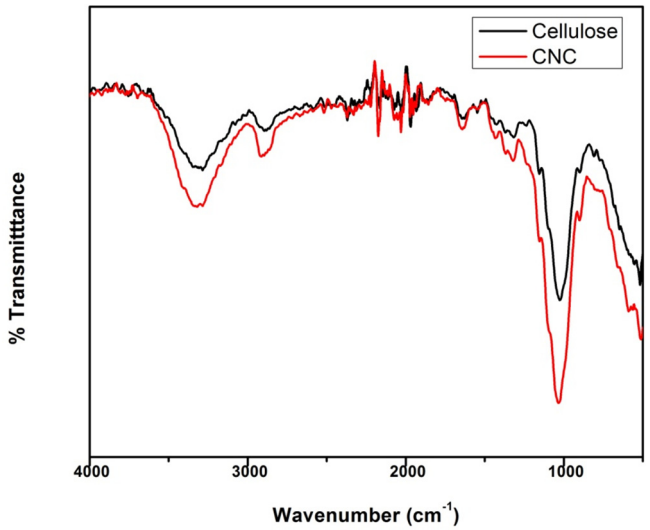

Fig. 4. ATR-FTIR spectra of (1) α-cellulose (2) cellulose nanocrystal.

3.2.3. X-ray diffraction (XRD)

It is used to study the crystalline behaviour and to evaluate the relation between the crystals structure and characteristics. Since cellulose in molecular structure is partially crystalline and partially amorphous, this means that the cellulose chains will be tightly held by mutual H-bonding in the crystalline (ordered) areas, whereas there is no H-bonding in the amorphous (disordered) areas of the cellulose chains. The size of crystallite and the crystallinity of cellulose are affected by chemical and mechanical treatments. To determine how the distinct chemical and mechanical treatments affect crystallinity, Crystallinity values were determined and compared between distinct treatments.

The XRD diffraction pattern of cellulose and CNC is shown in Fig. 5. The samples exhibited peaks at $2\theta = 16.5°$ and 22.5° and 34.6° at (1 1 0), (2 0 0) and (0 0 4) planes respectively which corresponds to the characteristic peaks of cellulose-I structure. The crystallinity index which was calculated according to amorphous subtraction method came out to be of 62.4% for α-cellulose and 76% for cellulose nanocrystals. The increase in the crystallinity index occurs during acid hydrolysis of cellulose (Fig. 5).

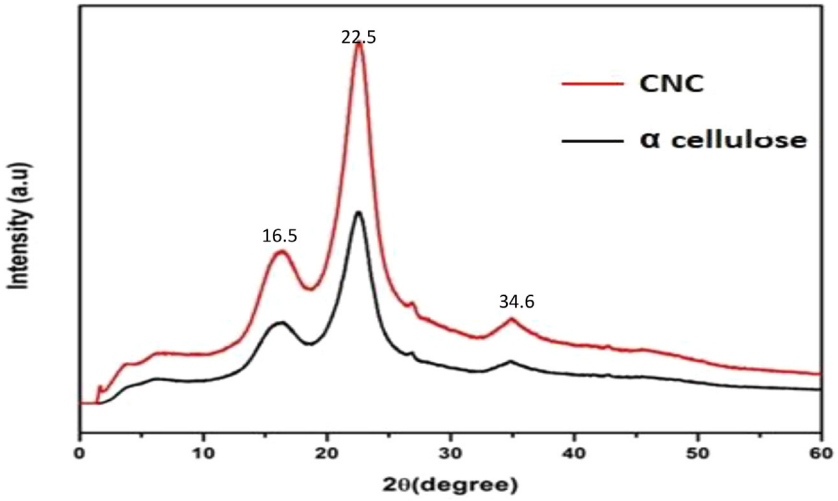

Fig. 5. XRD diffraction spectra of (1) cellulose nanocrystals (2) α cellulose.

3.2.4. High resolution-transition electron microscopy (HR-TEM)

To evaluate the diameters, TEM pictures of cellulose nanocrystals were used. The nanocellulose cellulose TEM micrographs (Fig. 6) disclosed that chemical and mechanical treatment resulted in clear rod shape CNC in the form of a network of nanocrystals (as confirmed by SEM picture Fig. 3) from the cell wall and separation of these nanocrystals from the micro size crystal bundles. The average crystal diameter was discovered in the 5–15 nm range. This outcome was consistent with previous studies [30–31]. TEM also observed a tendency of agglomeration. It is not apparent whether this was due to the elevated density of hydroxyl groups on the surface of molecules in the cellulose chain that favoured hydrogen bond formation or whether it represented the suspension state.

3.2.5. Thermal gravimetric analysis (TGA)

The TGA curve C of Fig. 7 showed that the decomposition temperature of CNC was higher than the α cellulose, respectively. The higher temperatures of the purified cellulose nanocrystals thermal decomposition and relatively low residue levels are related to the partial removal of hemicelluloses, lignin and pectin from the crystals, as well as the higher crystallinity of cellulose [32–33]. In all cases, due to the evaporation of material water or low molecular weight compounds, a small weight loss was found in the range of 35–150 °C. A peak change from 260 °C to 310 °C also occurred due to pyrolysis of cellulose and hemicelluloses.

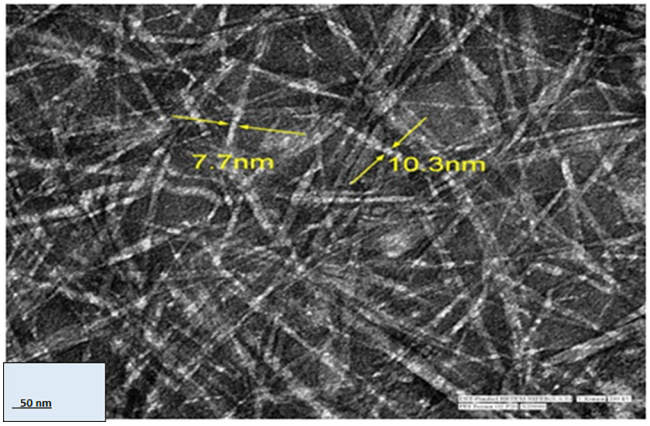

Fig. 6. TEM images of prepared nanocellulose showing size in the Nano dimension range.

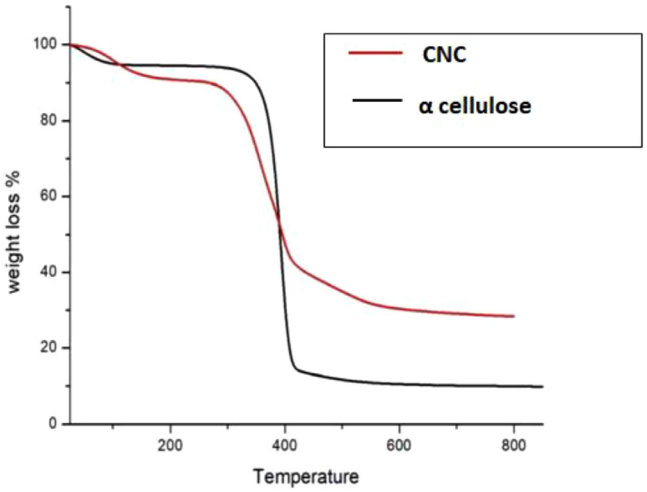

Fig. 7. TGA of alpha cellulose and cellulose nanocrystals.

4. Conclusions

Rice straw can be used to produce CNCs as a source of cellulose. Chemical treatments, i.e. acid-hydrolysis, was used to prepare CNCs. Methodology of the response surface, the central composite design is discovered to be helpful in defining the key variables. SEM, HR-TEM, described the morphology and topography of nanocrystals. SEM studies demonstrate supporting proof for Nano-scale CNCs with HR-TEM assessment. The average diameter of the CNCs was found in the range of 5–15 nm. FTIR-ATR has evaluated the structural modifications and XRD, and thermal analysis was measured by Thermal gravimetric analysis (TGA) which revealed that the decomposition temperature of CNCs was higher than the α cellulose. Hence, this studied revealed that preparation of CNCs from rice straw by acid hydrolysis method may be very effective process to be carried out at large scale.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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