

## Isolation of Nanocellulose from Rice Waste via Ultrasonication

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In this work, nanocellulose was obtained from rice husk and rice straw. Initially, the samples were subjected to different types of chemical treatment and the obtained purified cellulose fibers were separated using ultrasonication. Nanocellulose isolated by mechanical treatment has been characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Surface morphology and nanocellulose size studies using SEM and AFM revealed that there was a reduction in fiber diameter during ultrasonication. XRD results indicated that the crystallinity of nanocellulose was approximately 62% and 71% for rice straw and rice husk, respectively. The TGA curve of the isolated nanocellulose after ultrasonic treatment showed that the degradation behavior is quite similar to purified cellulose fibers, suggesting that the ultrasonic treatment had a slight effect on the thermal decomposition of the nanocellulose.

*Keywords:* Nanocellulose; Ultrasound; Cellulose; Rice husk; Rice straw

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### INTRODUCTION

Nanotechnology is one of the most important factors in global economic growth and prosperity in this century and makes new capabilities for materials, tools, and systems which will create a revolution in technology and industry. Nanotechnology is widely used in all fields. One of the most unique manufacturing nanomaterials are nanocelluloses. Nanocelluloses have unique properties, such as renewability and biodegradability; they are harmless to human health and can even be considered as appropriate alternatives to many petroleum products and other industrial products (Hubbe *et al.* 2008; Ioelovich 2008). Nanocelluloses are widely used in medicine and pharmaceuticals, electronics, membranes, porous materials, paper, and food because of their availability, biocompatibility, biological degradability, and sustainability. Availability and continuous and inexpensive sources of crude material is essential for the stability and development of this new industry (Hubbe *et al.* 2008; Ioelovich 2008; Kamel 2007). Agricultural wastes are additional materials from harvested crops that have different usages. Rice is one of the most important crops which is mostly grown in the north of Iran. The rate of production of rice in Iran is about three million tons of grain per year; for every ton of grain, about 1.5-2.1 tons of straw in the fields are extracted (Balalae *et al.* 2003; Bharadwaj 2004). Rice husk is the outer covering of the paddy and is considered to be a waste; it accounts for 20–25% of the rice grain's weight. It is removed during rice milling (Bharadwaj 2004). The main components of rice husk are cellulose

(25-35%), hemicellulose (18-21%), lignin (26-31%), and silica (15-17%) (Janardhnan 2011; Dufresne *et al.* 2000), and the main components of rice straw are cellulose (28-48%), lignin (12-16%), silica (9-14%), and wax (7.3%) (Faezipour *et al.* 2002; Shakeri *et al.* 2005). Nanocellulose can be obtained from various sources such as wood fibers (Abe *et al.* 2009), cotton (De Morais Teixeira 2010), potato tuber cells (Dufresne 2000), cladodes and spines from *Opuntia ficus-indica* (Malainine 2003), lemon and maize (Rondeau-Mouro *et al.* 2003), soybean (Wang *et al.* 2007), wheat straw and soy hulls (Alemdar *et al.* 2008), hemp fiber (Wang *et al.* 2007), coconut husk fibers (Rosa *et al.* 2010), branch-barks of mulberry (Li *et al.* 2009), pineapple leaf fibers (Cherian *et al.* 2010), banana rachis (Zuluaga *et al.* 2009), sisal (Moran *et al.* 2008), pea hull fiber (Chen *et al.* 2009), sugar beet (Dinand *et al.* 1999; Dufresne *et al.* 1997), and rice husk (Luduena *et al.* 2011; Rosa *et al.* 2011). Several processes have been used to extract highly purified nanofibers from cellulosic materials. These methods include mechanical treatments, such as cryocrushing (Chakraborty *et al.* 2005), grinding (Abe *et al.* 2009), and high-pressure homogenization (Nakagaito *et al.* 2004), chemical treatments, such as acid hydrolysis (Araki *et al.* 2000; Liu *et al.* 2010), biological treatments, such as enzyme-assisted hydrolysis (Hayashi *et al.* 2005; Henriksson *et al.* 2007) and TEMPO-mediated oxidation (Iwamoto *et al.* 2010; Saito *et al.* 2009) and synthetic and electro spinning methods (Frenot *et al.* 2007) as well as a combination of two or several of the aforementioned methods.

## EXPERIMENTAL

### Raw Materials

The rice husk (RH) and rice straw (RS) used in the present work consisted of residues from Mazandaran farms. RH and RS were extensively washed with distilled water to remove dust and other impurities. This operation was performed several times at room temperature followed by drying at 103 °C in an oven. Hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium chlorite (NaClO<sub>2</sub>), sodium bisulphate (Na<sub>2</sub>SO<sub>4</sub>) and a pH 4 buffer solution were purchased from Merck Corporation and were used for chemical treatment.

### Preparation of Purified Cellulose

The washed and dried RH and RS samples were subjected to different types of chemical treatments. Samples were stirred with 3% KOH at a weight ratio of 1:12 and boiled for 30 min, and the mixture was left overnight. The filtrate was washed with distilled water, and 10% (v/v) HCl was added (100 mL). Afterward, the lignocellulosic residue was treated with 0.7% (w/v) sodium chlorite at a ratio of 1:50 g solid/mL liquor at pH 4 and kept boiling for 2 h. The remaining solid was first treated with 5% (w/v) sodium bisulphate solution at room temperature for 1h using a solid to liquor ratio of 1 g/50 mL. Then, the samples were washed with distilled water and dried at 100 ± 2 °C in an oven until constant weight was reached. Samples were treated with 17.5% (w/v) sodium hydroxide (NaOH) solution at room temperature for 8 h using a solid to liquor

ratio of 1 g/50 mL and were washed and dried again as reported in the previous step (Luduena 2011).

### **Nanocellulose (NC) Production**

The chemically purified cellulose fibers extracted from the rice husk and straw fibers were soaked in distilled water (1%). Then, cellulose suspensions were sonicated for 15 min using an ultrasonic processor UW 3200 (Bandelin Electronic, Germany) at 20–25 kHz to isolate the nanocellulose. The ultrasonic treatment was carried out in an ice bath; the ice was maintained throughout the entire ultrasonication.

### **Morphology of Purified Cellulose Fibers and Nanocellulose**

#### *Atomic force microscopy (AFM)*

AFM was performed with an Easyscan2 Flex AFM probe microscope in air. Samples were prepared by dispersing 1 mg of nanofibers in distilled water in an ultrasonic bath for 30 min. A droplet of resulting solution was cast onto a microscopy slide and dried in a vacuum oven at 70 °C for 1 h. The AFM images were collected from dispersed nanocellulose.

#### *Scanning electron microscopy (SEM)*

The morphological study of the final nanocellulose fibrils was done using scanning electron microscopy. SEM micrographs of the nanocellulose surface were taken using the TESCAN VEGA scanning electron microscope operated at 15 kV. The samples were coated with gold to eliminate the electron charging effects.

#### *X-ray diffraction analysis (XRD)*

The XRD patterns of the untreated fibers and isolated nanocellulose were obtained with an X-ray diffractometer (X' Pert MPD, Philips, Holland) using Ni-filtered CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 30 mA. Scattered radiation was detected in the range of  $2\theta = 5\text{--}50^\circ$  at a scan rate of  $1^\circ/\text{min}$ . The crystallinity index of cellulose based materials was calculated as follows.

$$\text{Crystallinity} = (I_{\text{cry}} - I_{\text{am}} / I_{\text{cry}}) \times 100 \quad (1)$$

Where  $I_{\text{cry}}$  represents the crystalline part of the material.  $I_{\text{am}}$  is represents the amorphous part.

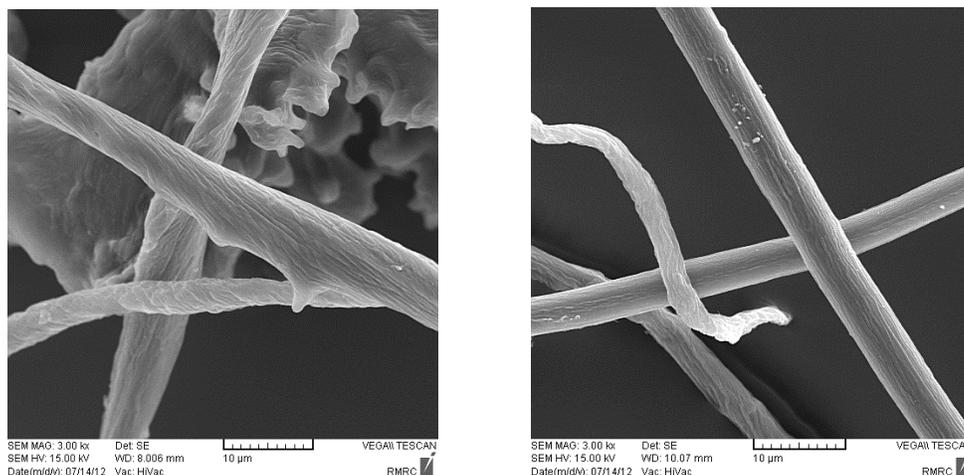
#### *Thermogravimetric analysis (TGA)*

The thermal stability of each sample was determined using a thermogravimetric analyzer (PL-TGA, Polymer Laboratories, England). The samples were heated from 25 to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

## **RESULTS AND DISCUSSION**

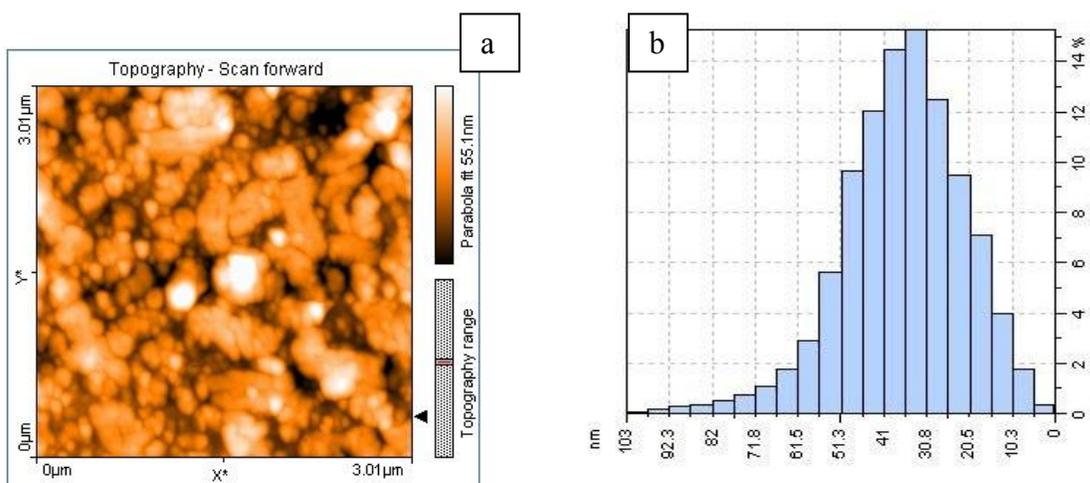
**AFM and SEM**

Studies of samples using the chemi-mechanical method by AFM and SEM and a size distribution diagram of the produced nanocellulose from rice husk and rice straw are shown in Figs. 1, 2, and 3. The average size of the obtained nanocellulose was 30-35 nm. Figure 1 shows the AFM image and distribution of the obtained nanocellulose from rice husk. The average size of the obtained nanocellulose was 26-29 nm.

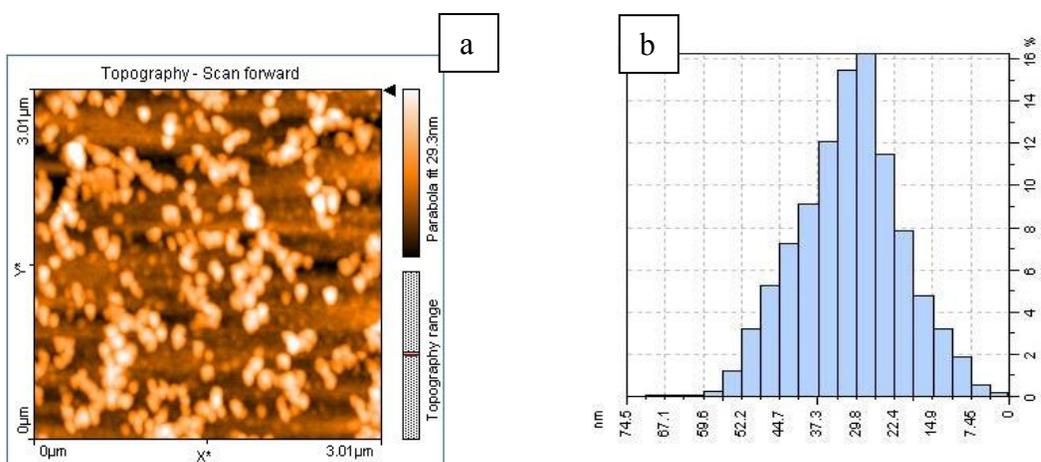


**Fig. 1.** SEM image of NC from RH (a), NC from RS (b)

Figure 2 shows the AFM image and distribution of the obtained nanocellulose from rice straw. In this study nanocellulose fibers were produced using a chemi-mechanical process, but in other research concerning wheat straw subjected to acid hydrolysis (Chen 2011), the length of the nanocellulose was the same length as the rice straw which was obtained in this research. However, Luduena *et al.* (2011) found that rice husk subjected to a chemical method led to a different result: the size range of nanocellulose was 4.6-12.4 nm. That is, the size of the particles was shorter than the nanocellulose from rice husk in this research, because the cellulose chain was broken more using the chemical method.



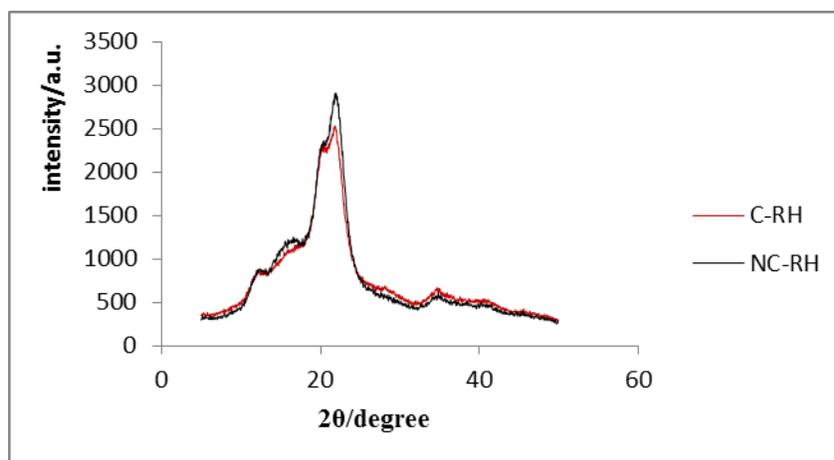
**Fig. 2.** AFM image of NC from RH (a), size distribution of NC from RH (b)



**Fig. 3.** AFM image of NC from RS (a), size distribution of NC from RS (b)

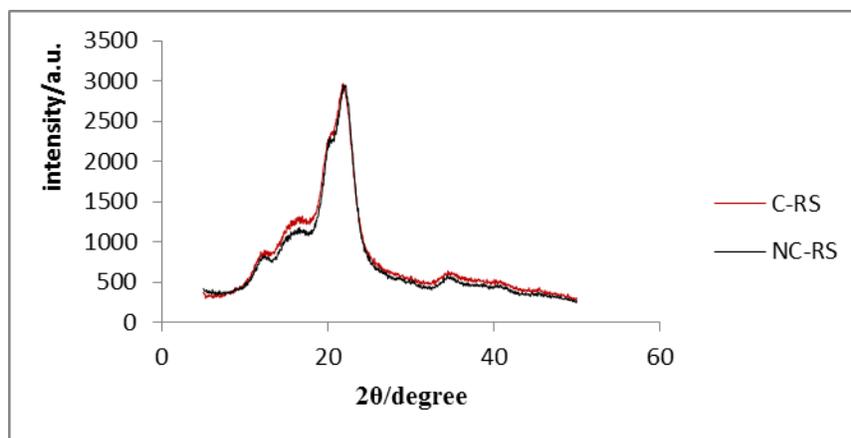
### X-ray Analysis

XRD studies of the treated and untreated cellulose fibers were performed to investigate the crystallinity of the fibers. Figures 4 and 5 and Table 1 show the equatorial X-ray diffraction patterns and the relative degrees of cellulose crystallinity, respectively.



**Fig. 4.** X-ray diffraction patterns of the cellulose and NC of rice husk

The crystallinity of the purified cellulose of rice husk and rice straw was 67% and 56%, respectively. Removal of the noncellulosic constituents of the fibers by chemical treatment will cause the crystallinity to change. The fiber constitutes crystalline and amorphous regions. Alkali treatment of the natural fiber will lead to the swelling of the fiber and a subsequent increase in the absorption of moisture. Treatment with alkali leads to the removal of cementing materials like lignin, hemicelluloses, and pectin which will result in the increase of percentage crystallinity of the fiber.



**Fig. 5.** X-ray diffraction patterns of the cellulose and NC of rice straw

The crystallinity in the RH nanocellulose was 71%. Rosa *et al.* (2011) obtained a crystallinity of 67% from RH nanocellulose using a chemical method. Luduena *et al.* (2011) produced nanocellulose using a chemical method, and the results of X-ray diffraction showed that the crystallinity of nanocellulose was approximately 76%. The crystallinity of nanocellulose was lower than the crystallinity of the unprocessed materials. A chemical method used to produce nanocellulose ultimately resulted in a loss of the amorphous structure of the cellulose chain. Consequently, the crystallinity resulting from the chemical method is more than that obtained using the mechanical

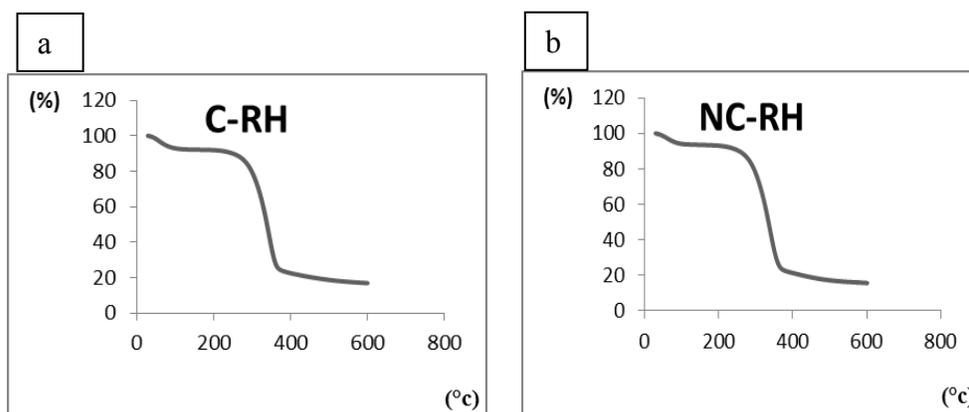
method, because the amorphous structure was not broken completely. Also, the crystallinity in the nanocellulose from RS was 62.79%. Chen *et al.* (2011) came to the same conclusion in research on wheat straw subjected to a mechanical method; the crystallinity of nanocellulose from wheat straw was 63.4%.

**Table 1.** Crystallinities of the Cellulose and NC from RH and RS

Source	Relative crystallinity (%)	
	Cellulose	Nanocellulose
Rice husk	66.79	70.9
Rice straw	56.13	62.79

### Thermogravimetric Analysis

Thermal decomposition parameters were determined from the TGA curves as described below at a heating rate of 10 °C/min. The TG curves of the untreated and the final nanocellulose of rice husk and straw are shown in Fig. 6(a) and (b). TG curves show several decomposition steps. In a nitrogen atmosphere, the main peak appears at around 350 °C and is due to the thermal decomposition for the pyrolysis of cellulose (Chen 2011; Luduena 2011).



**Fig. 6.** TG curves of C and NC from RH (a), RS (b) in nitrogen atmosphere

In the study of Chen *et al.* (2011), maximum weight loss was reached at 335 °C. The degradation temperatures of the nanocellulose isolated from the purified cellulose of rice husk and rice straw were found to be 348 and 350 °C, respectively. In all cases, a small weight loss was found in the range of 40-180 °C due to the evaporation of the humidity of the materials or the low molecular weight compounds remaining from the isolation procedures (Chen 2010). The higher temperatures of the thermal decomposition of the purified cellulose fibers are related to the partial removal of hemicelluloses, lignin, and pectin from the fibers, as well as the higher crystallinity of cellulose (Abe 2009). The TG curve of the isolated nanocellulose after ultrasonic treatment displayed a degradation behavior that is highly similar to that of the purified cellulose fibers, suggesting that the ultrasonic treatment had little effect on the thermal decomposition of the nanocellulose (Chen 2011). The high thermal properties of the nanofibers may broaden the fields of

application of cellulose fibers, especially at temperatures higher than 200 °C for biocomposite processing.

## CONCLUSIONS

Purified cellulose of rice husk and rice straw was obtained from several chemical treatments. Nanocellulose was isolated from purified cellulose fibers by chemical treatments followed by ultrasonic fibrillation. Nanocellulose with diameters ranging from 30 to 35 nm for RH and 26 to 29 nm for RS. The crystallinity of nanocellulose was 70.9 and 62.79% for RH and RS, respectively. The TG curve of the isolated nanocellulose after ultrasonic treatment showed a degradation behavior that is highly similar to the purified cellulose fibers, suggesting that the ultrasonic treatment had little effect on the thermal decomposition of the nanocellulose. The obtained nanocellulose may be potentially applied in various fields, such as bionanocomposites, filtration media, and packaging.

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