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Extraction of Cellulose Micro Sheets from Rice Husk: A Scalable Chemical Approach

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ABSTRACT

A two step methodology is reported to extract the micro size cellulose from rice husk by chemical treatment. The chemically extracted cellulose is micronised into micro dimensions under ambient conditions through the controlled degradation of amorphous segment present in cellulose chain by acid hydrolysis. The obtained cellulose was characterized by infra red spectroscopy, X- ray diffraction and scanning electron microscopy. These techniques reveal the crystalline nature of micro size cellulose having particle size in the range from 180- 250 nm.

Keywords: Biomass, Rice husk, Acid hydrolysis, Micro cellulose sheet

INTRODUCTION

The rice husk (RH) is the residual biomass of paddy crop (1-2). It contains 35% cellulose, 25% hemicellulose, 20% lignin and 17% ash (3-5). The RH composites with biodegradable polymer like poly lactic acid, poly butylene succinate find applications in automobile, building construction profile, textile, pharmaceutical industries (6-8). The reactive surface of -OH side group of micro structured cellulose facilitates the grafting with other molecules (9). Such surface functionalization of cellulose makes it suitable for fabrication of energy efficient devices, biomedical implants, semiconductor devices, sensor, packaging films, etc (10-11). The cellulose extracted from RH is suitable for drug delivery (12) and water decontamination (13). The present paper reports a two step procedure to extract micro sized cellulose crystals from the RH. The morphology and structure of cellulose extracted from RH have been investigated.

METHODOLOGY

The chemicals like sodium hydroxide, potassium hydroxide, sodium carbonate and potassium carbonate of E- Merk brand (AR grade) were used along with the RH from local market.

Isolation of Chemically Purified Cellulose

The chemically purified cellulose was isolated from the RH using earlier our reported methods (13). In brief, the finely grounded RH was cleaned in distilled water, stirred to remove impurities and dried at 100^0C. It was then treated with 5% NaOH (aq) and stirred on a magnetic stirrer for 45 minutes. It was then left to dry overnight. The slurry was filtered. Its liquid part consisted of lignin and silica while residue contained cellulose. The residue was dried in air-circulated oven at 105°C for 6 h and then stored in air tight polybags.

Extraction of cellulose crystals

The above residue was converted into cellulose crystals by acid-hydrolysis (14-15). The acid hydrolysis was done with 64% (w/w) H_2SO_4 solution, 1:10 g/ml (cellulose: dilute H_2SO_4) at ambient temperature for 60 min under constant mechanical stirring on a magnetic stirrer. The hydrolysis reaction was quenched by adding chilled distilled water (ten times) followed by successive centrifugation at 2000 rpm for 15 min to remove acidic solution. The sediments were collected, re-suspended and dialyzed against distilled water until pH 6-7 was reached. After this, the sample was again centrifuged and then sonicated for 10 min in an ice bath.

Chemical and Morphological Testing

The samples were investigated using Perkin Elmer (RK-1310) Fourier transform infra red (FTIR) spectrometer. The samples were dried in oven at 105°C for 4-5 h, then mixed with KBr in a ratio of 1:200 (w/w) and pressed at 10 ton to form pellets. The spectrum was recorded in the absorbance mode in the wavelength range of 4000 - 400 cm^{-1}.

The structure of samples was evaluated by using a Rigaku (RH- 200BH) model X- ray diffractometer. The parameters were -scanning rate of 2° per min with Cu- Kα radiation source ($\lambda = 1.54060$ Å) operating voltage of 40 kV and current 30 mA. The X-ray diffraction (XRD) patterns were obtained over the angular range $2\theta = 5- 60^o$. The crystal size of cellulose structure in respect of (200) plane was calculated using the well known Scherrer equation**:**

$$t = k * \lambda / (\beta * \cos \theta) \qquad (1)$$

where; k is the correction factor, λ is the wavelength, θ is the diffraction angle and β is the corrected angular width (in radians) at half maximum intensity. The correction factor k is usually taken to be 0.91. The crystalline size was found to be in the range of 185 nm.

The surface morphology of cellulosic fibers and extracted cellulose was examined using scanning electron microscope (SEM) of Hitachi make (model 3700) at an accelerating voltage ranging in between 15-20 Kv. The surface morphology images of RH, alkali treated RH and extracted cellulose were taken at different magnifications.

RESULTS AND DISCUSSION

Concentration and Extraction

The isolation of the cellulose from the RH is shown schematically (Figure-I). The bleaching treatment of extracted cellulose with sodium chlorite ($NaClO_2$) removed lignin and tannins in scalable manner. These components were essentially responsible for the brown color of the RH. During the bleaching treatment, chlorine and chlorites rapidly oxidize lignin, to generate hydroxyl, carbonyl and carboxylic groups. These groups facilitate lignin solubilization in alkaline medium and also support cellulose purification (16).

The chemical treatment of cellulose using sodium chlorite solution at acidic pH ~5.0 for 45 min removed most of the lignin and solubilized hemicellulose (17). While, acid hydrolysis breaks the amorphous segment of cellulose and also miniaturizes the cellulose dimensions.

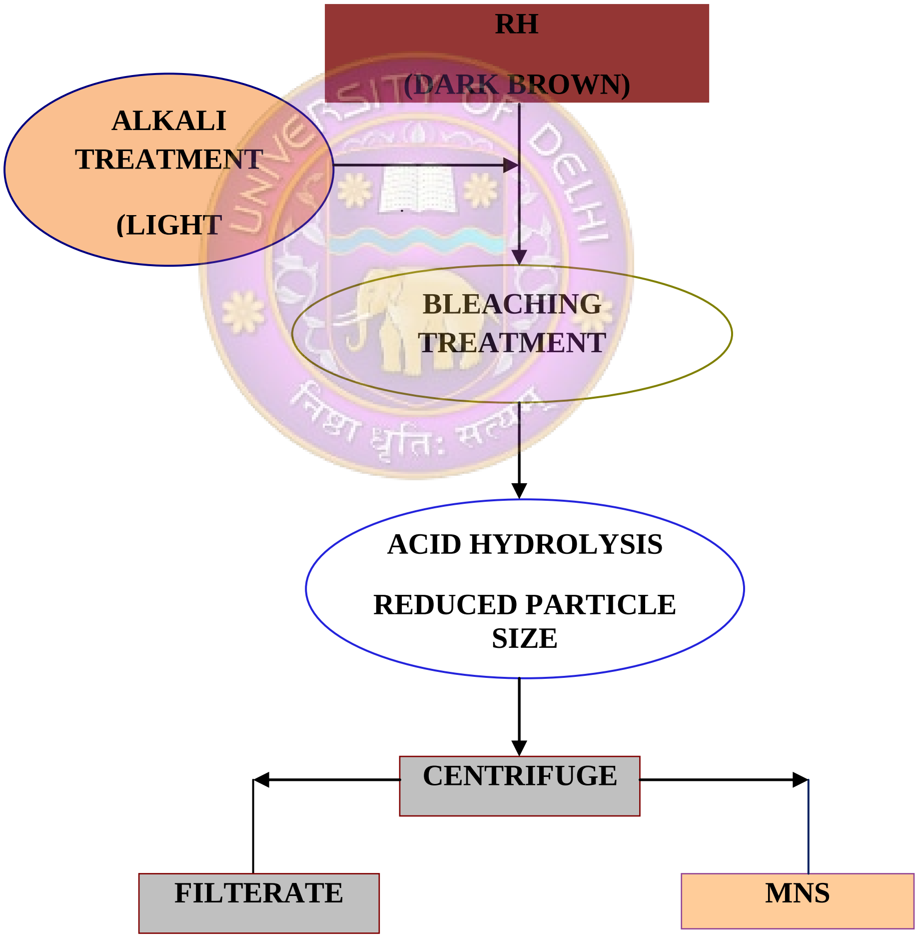

Figure-I Schematic representation for extraction micro size Sheet

Infrared Spectra:

FTIR spectral analysis of RH, alkali treated RH and extracted cellulose helps to understand the changes in molecular structure of RH during the both extraction steps. The FTIR spectra of the RH, alkali treated RH and extracted cellulose is shown in Fig-II. The broad absorption peak in the range 3600-3300 cm^{-1} reveals the presence of hydroxyl (OH) groups and the hydrophilic nature of samples. The peak at 2916 cm^{-1} is due to the C-H stretching vibration of cellulose. A shoulder type of peak at around 1700 cm^{-1} in the spectrum of the RH indicates the presence of acetyl or ester linkage of lignin component (18). This peak disappears in the spectra of extracted cellulose due to the removal of non cellulosic components. The peak at 1636 cm^{-1} due to C=O in the spectrum of the RH gets shifted to 1651 cm^{-1} in cellulose. It again shows the removal of hemicellulose (19). The effect of bleaching on RH can also be understood by IR analysis. The band near 1049 cm^{-1} in RH loses its intensity in cellulose sample. This band is due to the presence of xylans associated with hemicellulose in RH. The evolution of small but sharp peak at 973 cm^{-1} in the spectra of cellulose reveals its structure due to the glycosidic type C-H deformation. This peak also supports the b-glycosidic linkage between the anhydroglucose units in cellulose and also indicate the change in structure of cellulose (20).

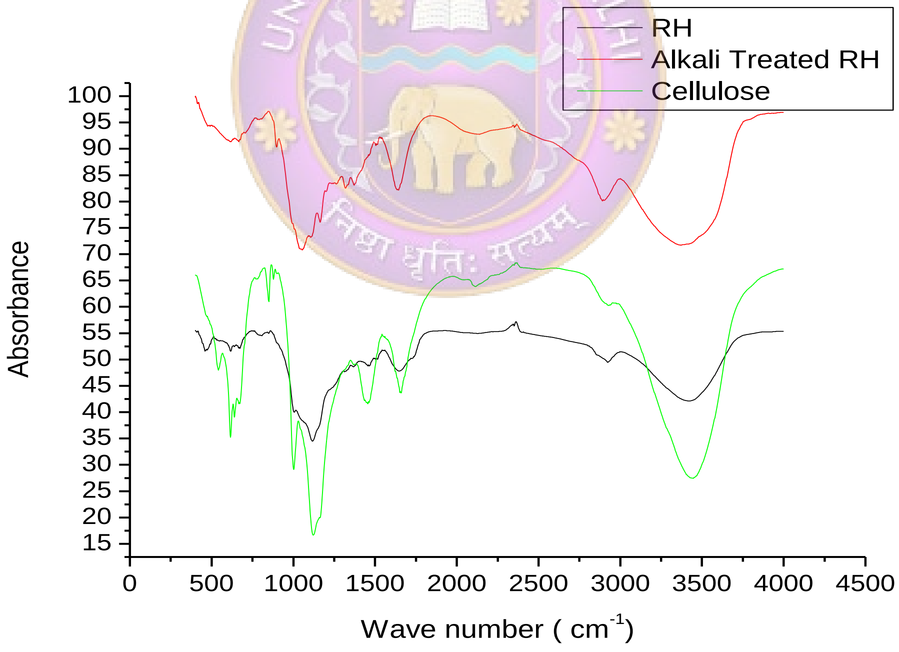

Figure-II FTIR of RH, alkali treated RH and extracted Cellulose

XRD

The XRD of the extracted cellulose and RH (Figure-II) shows that former is more crystalline in nature. The increased crystallinity of extracted cellulose is due to the removal of hemicellulose and lignin from RH (18). The large number of peaks in RH is due to its multi-component nature. However, the XRD of extracted cellulose compares with the reported diffraction (21). The broad peaks at $2\theta = 16^{0}$ and $2\theta = 22^{0}$ indicate typical cellulose I structure. The peak intensity at 22^{0} has been used to compare the degree of crystallinity employing Segal formula. The result reveals the 183% higher crystallinity of the extracted cellulose (21).

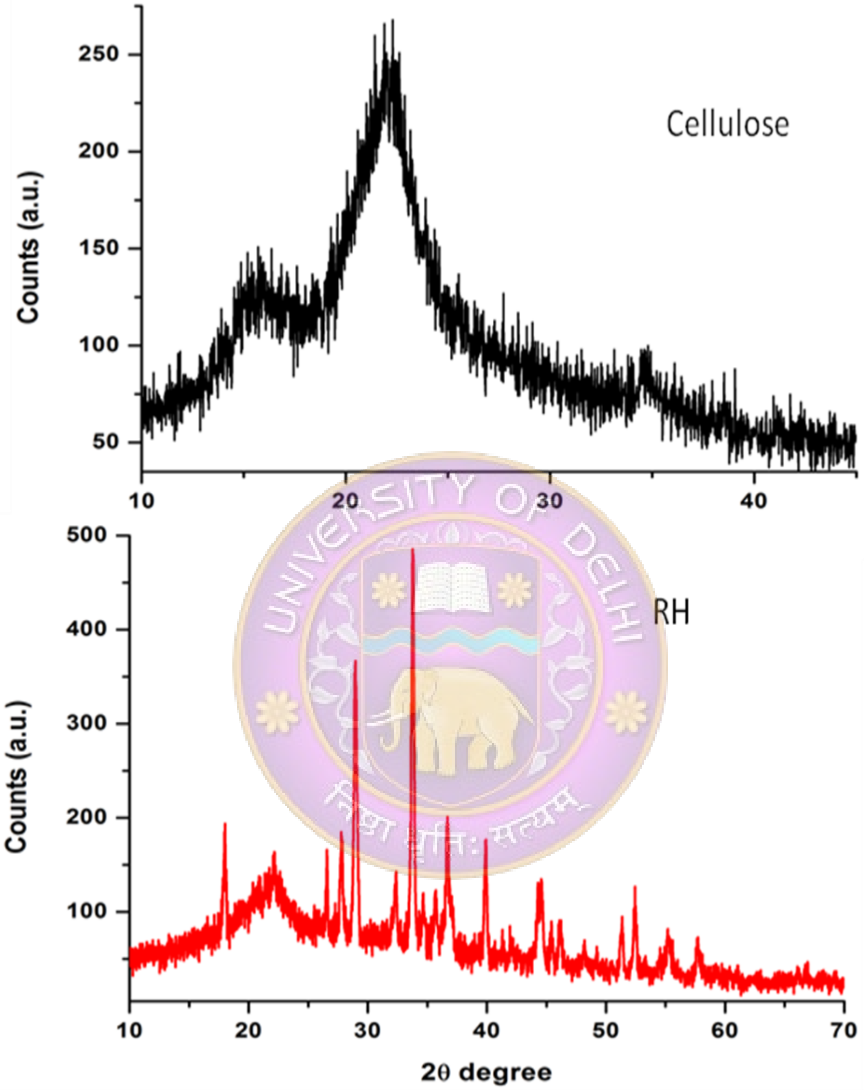

Figure-III XRD of Cellulose and RH

Morphological Study

The optical photographs of RH, alkali treated RH and extracted cellulose are shown in Fig- IV. The white colour of extracted cellulose (Fig IVA) is attributed to the elimination non cellulosic components.

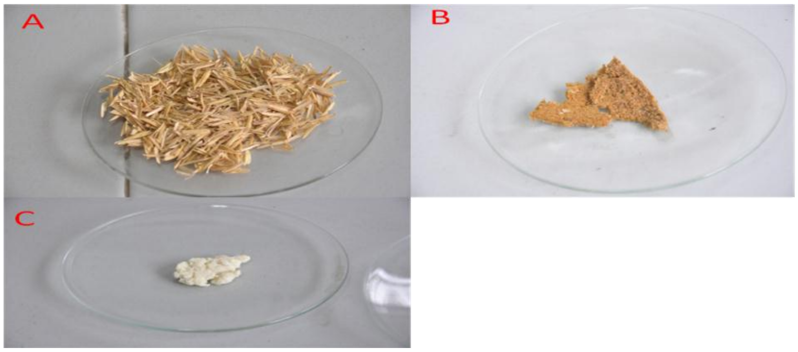

Figure-IV Optical photographs (A) RH (B) Alkali treated RH (C) Cellulose

The SEM photographs show smooth surface of RH epidermis (Fig. 5A) having an identical morphology as reported earlier (21).The removal of non cellulosic parts makes its surface rough (Fig-VB) and also decreases the particle size. Further, the acid hydrolysis degrades the less stable amorphous segment of obtained cellulose and in the process leads to the formation of cellulosic microsheets, (Fig-5C).

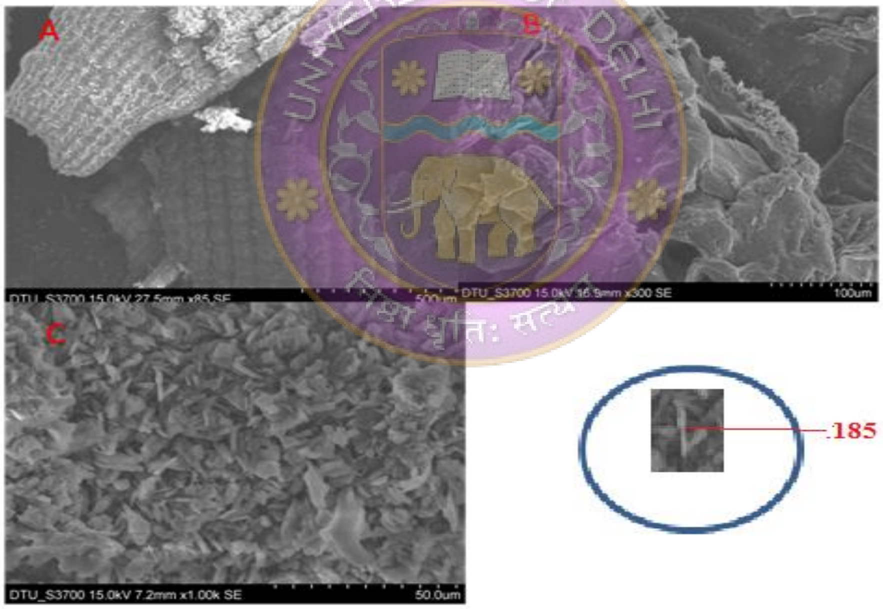

Figure-V SEM of (a) RH (b) Alkali treated RH (c) extracted Cellulose

CONCLUSION

The cellulosic microsheet having the thickness ranging from 180 to 250 nm, was successfully isolated from the agro waste RH. The crystallinity of the obtained cellulose increased effectively by 183%. The FTIR spectra confirmed the removal of non cellulosic components (hemicellulose, lignin, wax etc.) from the extracted cellulose.

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REFERENCES

1. Athinarayanan, J., Periasamy, V. S., Alhazmi, M., Alatiah, K. A., Alshatwi, A. A. (2015). Synthesis of biogenic silica nanoparticles from rice husks for biomedical applications. *Ceramics International,* 41: pp(275-281).

2. Davis, G. and Song, J. H. (2006). Biodegradable packaging based on raw materials from crops and their impact on waste management. *Industrial Crops and Products*, 23:pp(147-161).

3. Wang, L., Schnepp, Z., and Titirici M. M. (2013). Rice husk-derived carbon anodes for lithium ion batteries. *J. Mater. Chem.* 1*:* pp*(* 5269-5273).

4. Ishak, Z. A. M. (2011). Rice husk: Turning wastes into wealth. *eXPRESS Polymer Letters*, 5:pp(569).

5. Premalal Hattotuwa, G. B., Ismail and H., Bharin, A. K. (2002). Comparision of the mechanical properties of rice husk powder filled polypropylene composites with talc filled polypropylene composites. *Polymer Testing*, 21:pp(833-839).

6. Shukla, S. K. and Tiwari, A. (2010). *In Polysaccchrides: Development, Properties and Application, ed. Ashutosh Tiwari,* Nova Science Publisher Inc. N.Y.

7. Czaja, W. K., Young, D. J., Kawecki, M. and. Brown Jr., R. M. (2007). The future prospects of microbial cellulose in biomedical applications. *Biomacromolecules,* 8:pp(1-12).

8. Shukla, S. K. (2012). Synthesis of polyaniline grafted cellulose suitable for humidity sensing. *Ind. J. Eng. Mat. Sci*.,19:pp(417-420).

9. Chen, W., Yu, H., Liu, Y., Hai, Y., Zhang, M. and Chen, P. (2011). Isolation and characterization of cellulose nanofibers from four plant cellulose fibers using a chemical-ultrasonic process. *Cellulose,* 18 : pp(433-442).

10. Moon, R. J., Martini, A., Nairn, J., Simonsen J., Youngblood, J., (2011). Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem. Soc. Rev.*, 40, :pp(3941-3994).

11. Shukla, S.K., (2013). Synthesis and characterization of polypyrrole grafted cellulose for humidity sensing. *International Journal Biological Macromolecules,* 62,:pp(531-536)

12. Shukla, S.K., Nidhi, Sudha, Pooja, Namrata, Charu, Akshay, Silvi, Manisha, Rizwana, Bharadvaja, A., and Dubey, G. C. (2014). Metal Decontamination from Chemically Modified Rice Husk Film. *Adv. Mat. Lett.* 5 (6) :pp(352- 355).

13. Shukla, S.K., Nidhi, Sudha, Pooja, Namrata, Charu, Akshay, Silvi, Manisha, Rizwana, Bharadvaja, A., and Dubey, G. C. (2013). Preparation and Characterization of Cellulose Derived from Rice Husk for Drug Delivery. *Adv. Mat. Lett*. 4 (9),:pp(714-719).

14. Beck-Candanedo, S., Roman, M., and Gray, D. G. (2005). Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. *Biomacromolecule*s, 6:pp(1048-1054).

15. Bondeson, D., Mathew, A., and Oksman, K. (2006), Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. *Cellulose,* 13 (2):pp(171 - 180).

16. Dufresne, A., Cavaille, J-Y. and Vignon, M. R. (1997). Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils. *J. App. Poly. Sci*. 64 (6):pp(1185-1194).

17. Sun, J. X., Xu, F., Sun, X. F., Xiao, B. and Sun, R. C (2005). Physico-chemical and thermal characterization of cellulose from barley straw. *Polym. Degrad. Stab*. 88 (3):pp (521-531).

18. Cherian, B. M., Pothan, L. A., Nguyen-Chung, T., Mennig, G., Kottaisamy, M. and Thomas S. (2008). A novel method for the synthesis of cellulose nanofibril whiskers from banana fibers and characterization. *J. Agric. Food Chem*. 56 (14):pp(5617-5627).

19. Wang, B., Sain, M. and Oksman, K. (2007). Study of Structural Morphology of Hemp Fiber from the Micro to the Nanoscale. *Appl. Compos. Mater.* 14 (2):pp(89-103).

20. Alemdar, A. and Sain, M. (2008). Biocomposites from wheat straw nanofibers: Morphology, thermal and mechanical properties. *Compos. Sci. Technol.* 68 (2):pp(557-565).

21. Simone, M. L, Rosa, Noor Rehman, Maria Inez G. de Miranda, Sonia, M. B., Nachtigall, Clara, I. D. Bica (2012), Chlorine-free extraction of cellulose from rice husk and whisker isolation, *Carbohydrate Polymers* 87,: pp(1131-1138).

22. Rosa, M. F., Medeiros, E. S., Malmonge, J. A., Gregorski, K. S., Wood, D. F., Mattoso, L. H. C., Glenn, G., Orts, W. J. and Imam, S. H. (2010). Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohydr. Poly*. 81 (1)☹ 83-92)