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Synthesis and Characterization of Cellulose Based Nanofibres from Rice Husk

Onoja, D.A.[1], Ahemen, I.[2], Iorfa, T. F.[3]
[1-3]Dept. of Physics.University of Agriculture, Makurdi
Corresponding Author: Iorfa, T.F.

Abstract: *In this research work, nanocellulose was isolated from rice husk. The sample was initially subjected to several chemical treatments. The isolated nanocellulose has been characterized by Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Fluorescence (ED-XRF), X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The surface morphology and size of nanocellulose have been determined to be in the range of 8-25nm. The fourier transform infrared (FTIR) result shows that silica and other lignocellulosic components of the rice husk have been eliminated. The XRF table shows the elemental constituents of the untreated rice husk and EDS profile reveals that silica and other components of the rice husk have been eliminated after undergoing series of chemical treatments leaving high content of nanocellulose. The XRD analysis shows the characteristics of amorphous nanocellulose. The obtained results will be useful both from technological and academic point of view, especially for people working in the area of biodegradable nanocomposite. Finally, the final material could be of added value to raw biomass material source particularly rice husk.*

Key words: *Rice husk; chemical treatment; morphology; nanocellulose fibres*

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I. Introduction

In recent years the production of more sustainable and environmental friendly materials has gain the attention of researchers. This includes the search for alternative to petroleum-based materials from agro-waste materials. One of the most unique manufacturing nanomaterials is nanocellulose. Nanocellulose has unique properties such as renewability and biodegradability; they are harmless to human health and other industrial products (Hubbe *et al.*, 2008). Nanocellulose is widely used in medicine and pharmaceuticals, electronics, membranes, porous materials, paper and food because of its availability, biocompatibility, and biological degradability. Availability and continuous and inexpensive sources of the crude materials is essential for the stability and development of this industry (Karmel, 2007).

One of the potential agro-wastes is rice husk (RH) which is available in large quantity as a waste from rice milling industries (Shukla *et al.*, 2013). Rice husk is the outer covering of the paddy and is considered to be a waste. The composition of ice husk is about 35% cellulose, 25% hemicelluloses, 20% lignin 17% ash (which is mainly 94% silica by weight) and 3% wax. Rice husk is removed during rice milling (Bharadwaj *et al.*, 2004). The collection and disposal of rice husk is difficult and generally left unused or simply burnt as crude source of energy. The advantageous feature of rice husk is its renewable nature, low density and nonabrasive with reasonable strength and stiffness.

The basic constituent of rice husk which is cellulose is thermodynamically stable, crystalline structure with numerous hydrogen bonds. Cellulose was discovered by a chemist,Anselme Payen in 1839. He isolated cellulose from plant matter determined its chemical formula. The nanocellulose fibres are made with ether or esters of cellulose, which can be obtained from the bark, wood or leaves of plants or plant-based materials (Stefani *et al.*, 2005; Ruseckaite*et al.*, 2007; Zuluaga *et al.*, 2009). Several routes have been used to isolate microfibrils from natural resources such as sisal (Moran *et al.*, 2008), hemp (Wang *et al.*, 2007) lemon and maize (Rondeau-Mouro *et al.*, 2003). The cellulose nanofibres have been shown to be useful as new reinforcing agents in the production of nanocomposites (Faria *et al.*, 2006; Zuluaga *et al.*, 2007)

Due to the abundance of rice husks in Nigeria particularly in Makurdi rice milling industries and the interest of scientists to use technology to recycle agro-wastes, it is therefore useful to consider the use of rice husk for producing value-added products particularly nanocellulose fibres and provide a clear positive effect on the environment.

II. Materials And Method

Materials

The materials required for this research work includes; Rice husk(RH) from wurukum (Makurdi, Benue State) rice mill, water, Sodium hydroxide(NaOH), hydrochloric acid (HCl), sodium chlorite ($NaClO_2$), disodium tetraoxosulphate (vi) (Na_2SO_4), potassium hydroxide (KOH), tetraoxosulphate (vi) acid (H_2SO_4), buffer solution ρH4, beakers(250ml, 600ml, 1000ml), volumetric flask, stirrer, sieve, crucibles, measuring cylinder (500ml & 1000ml) filter paper, hemaltic plastic and refrigerator.

Methods

Rice Husk Treatment

The rice husk was collected from rice mill industry Wurukum, Makurdi. The rice husk was extensively washed with deionized water for 30mins to remove dust and other impurities. The colour of the rice husk sample at this stage was light brown. The rice husk was dried in an oven at a temperature of 100^oC. The washed and dried rice husk sample(S_0) was subjected to different chemical treatments.The rice husk sample (S_0) was first boiled with 5% (wt) NaOH ratio 1:12g for 1hr and was allowed to stay for 48hrs after boiling. The NaOH removed part of the inorganic fraction of the rice husk (mainly silica). The colour of the sample at this stage remains dark brown which indicates the presence of lignin, wax and hemicellulose. After the 48hrs, the sample was washed twice with deionized water and was treated with 10% (v/v) HCl (100ml) for 1hr.The formed precipitate of silica was separated from organic residue. The action of the HCl on the sample also removed the hemicellulose (S_1). Afterward the lignocellulosic residue was boiled with1.0 %(w/v) $NaClO_2$ solution at a ratio of 1g: 50ml with a buffer solution of ρH4 for two hours. The bleaching treatment of the sample with sodium chlorite ($NaClO_2$) removed part of the lignin and wax in a scalable manner. The components are responsible for the brownish colour of the sample. During the bleaching treatment, chlorine and chlorite rapidly oxidized lignin to generate hydroxyl, carbonyl and carboxylic groups.

The boiled sample was treated with 5 %(w/v) Na_2SO_4 and stirred continuously for 1hr at a ratio of 1g: 50ml. The Na_2SO_4 treatment caused partial removal of residuals of lignin and waxes. The colour of the sample at this stage remains light yellow. The sample was then washed with deionized water and dried at 100^oC in an air circulated oven until it constant weight was reached (S_2). After that, the sample was treated with 18% (w/v) KOH solution at a room temperature using a solid liquor ratio 5g/250ml and was left undisturbed for 24hrs.The KOH purified the cellulose and transformed it from cellulose 1 to cellulose 2.The alkaline treatment with KOH caused the complete removal of lignin and waxes and improved the lightness of the sample which indicates that the resultant sub-product could be mainly cellulose. The sample was washed with deionized water and dried in an oven at a temperature of 100^oC (S_3). The sample was then treated with 75% (wt) H_2SO_4 and continuously stirred for about 10mins and washed with cold deionized water in order to stop the reaction of the sulphuric acid. The colour of the sample at this stage was white which was due to the elimination of the non-cellulosic component of the rice husk. After washing, the sample was filtered and allowed to stay overnight at room temperature before it was finally dried in an air circulated oven at a temperature of 40^0C (S_4).The acid hydrolysis broke the amorphous segment of the cellulose and also miniaturized the cellulose dimension. Below is the flow chart of the treatment that was carried out.

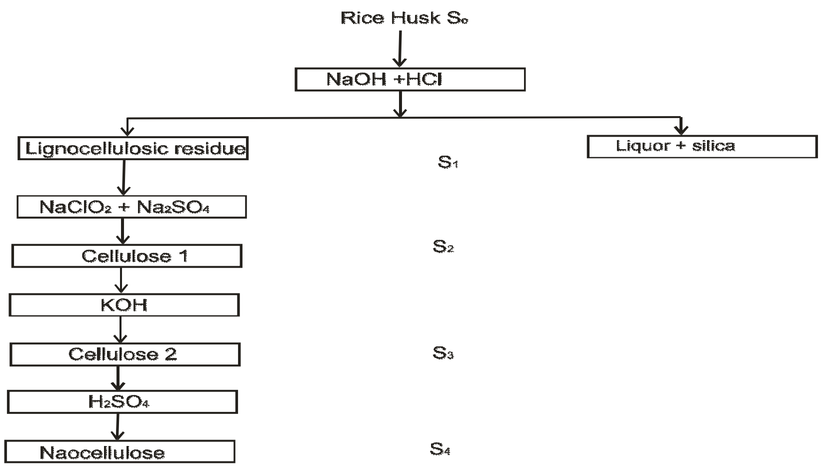

Figure 1: Scheme of chemical treatment of rice husk.

SEM
SEM analyses were performed with Oxford PhenomProx SEM (ABU, Zaria) and Tescan VEGA 3 SEM (UFS. UV, South Africa) to observe the morphology and size of the nanocellulose fibres. The surfaces were coated with 149.4nm carbon. The sample was observed using an accelerated voltage of 20KV.

ED-XRF
The chemical composition of the rice husk and nanocellulosefibres were determined with XRF Xsupreme800 Phenomworld(ABU, Zaria) and Oxford X Max EDS (UFS. UV, South Africa).

FTIR
The FTIR was performed with Cary 630 Agilent Technologies (ABU, Zaria) to determine the infrared spectrum emission of the rice husk and nanocellulose fibres.

XRD
The XRD was performed with Bruker D-8 Advanced diffractometer (ABU, Zaria)to determine the microstructure of the rice husk and nanocellulose fibres.

III. Results And Discussion

Chemical Composition

The chemical composition of the rice husk and nanocellulose fibres are given in table 1 and figure 3 below respectively.

Element	Concentration
Na2O	0.000 Wt %
MgO	2.813 Wt %
Al2O3	2.056 Wt %
SiO2	71.472 Wt %
P2O5	14.575 Wt %
SO3	3.159 Wt %
Cl	0.739 Wt %
K2O	2.417 Wt %
CaO	1.088 Wt %
TiO2	0.186 Wt %
Cr2O3	0.003 Wt %
Mn2O3	0.479 Wt %
Fe2O3	0.921 Wt %
ZnO	0.091 Wt %
SrO	0.000 Wt %

Table 1: Chemical Composition of rice husk

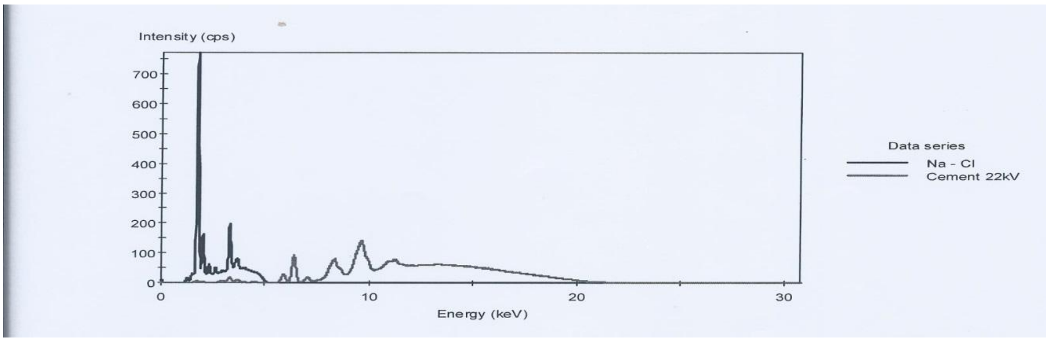

Figure 2: XRF profile of rice husk

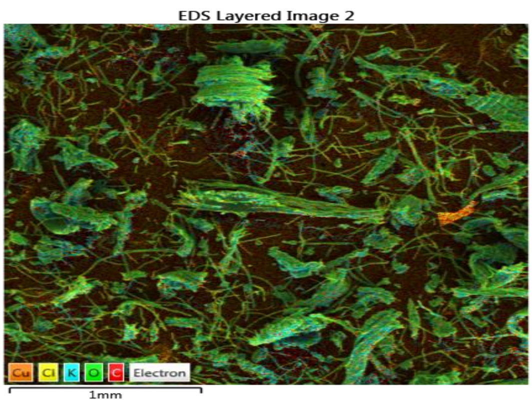

Plate 1: EDS image of nanocellulose

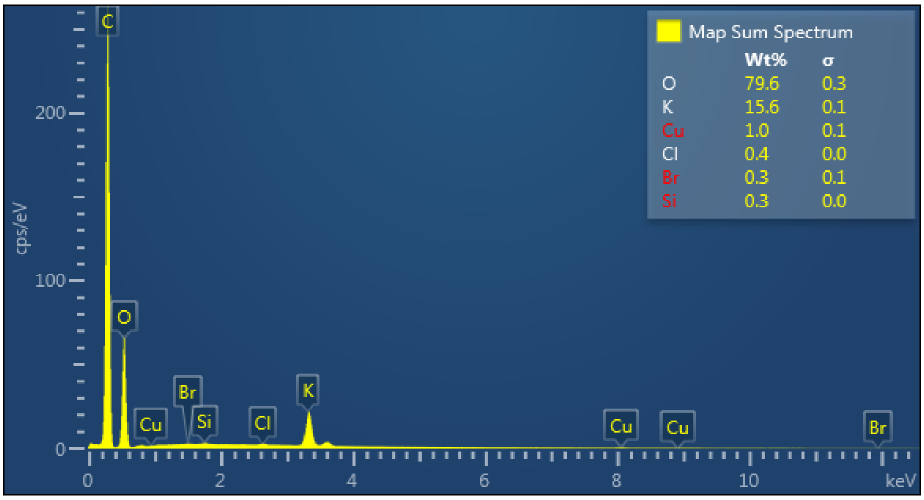

Figure 3: EDS profile of nanocellulose

From table 1 above, it shows that the rice husk constitutes about 33wt% silica. The figure 2 shows the XRF profile of rice husk. The peak above 700cps represents silica.The EDS profile in plate 1 and figure 3 shows the constituent elements of the nanocellulose. The highest peak corresponds to C follow by the peak which represent O. Other smaller peaks include Cu, Br, Si, K, and Cl.

The EDS of the extracted NC (figure 3) shows that the non-organic component of the rice husk silica has been eliminated leaving a very negligible content. It also shows that other organic components like lignin,hemicellulose and wax have been removed leaving high content of the cellulose.

Morphological Study

The optical photograph of rice husk treatment is shown in plate 2 below. After series of chemical treatment, the brownish colour of the rice husk sample changes to white. The white colour of the nanocellulose indicates the elimination of the noncellulosic components of the rice husk.

Plate 2: Optical photograph of Rice husk treatment

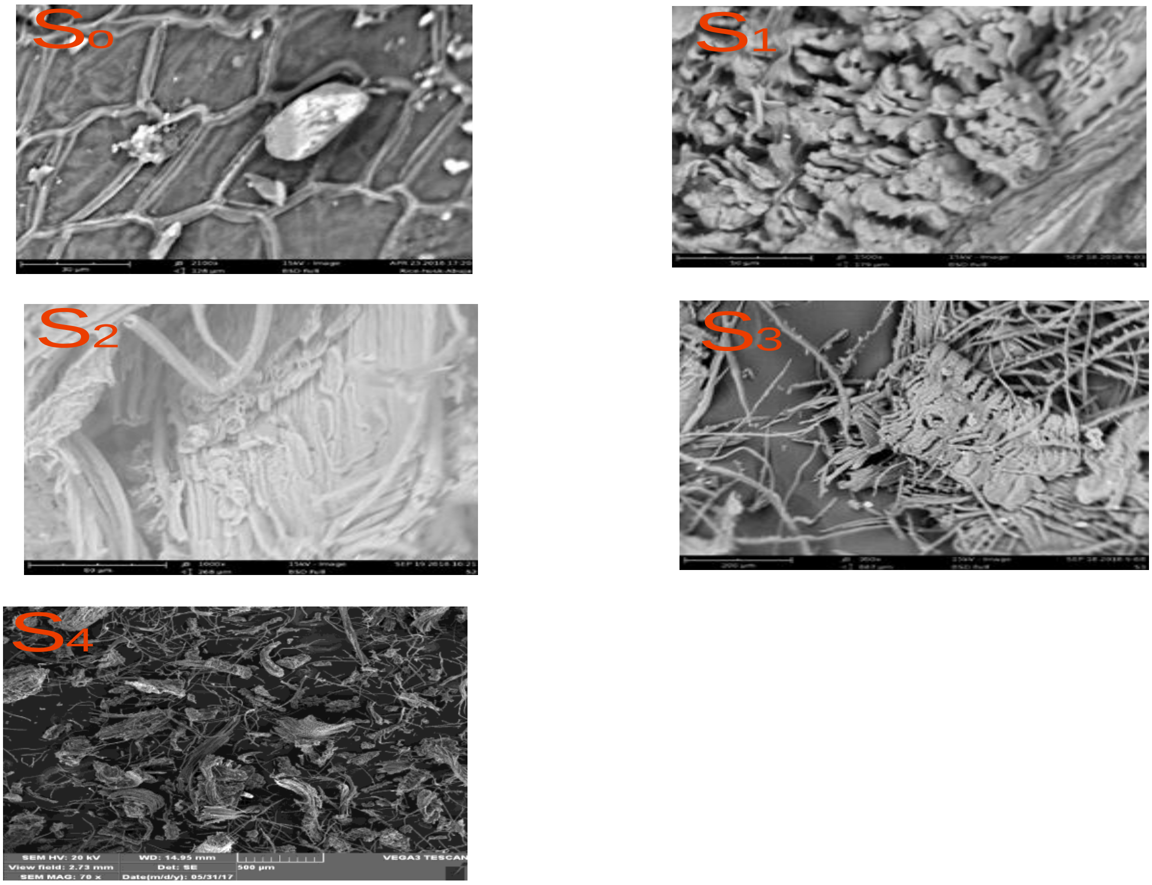

Plate 3: SEM images of (S_0) untreated rice husk, (S_1) treated with (NaOH + HCl), (S_2) treated with ($NaClO_2$ + Na_2SO_4), (S_3) treated with (KOH) and (S_4) treated with (H_2SO_4)

The plate 3 (S_0) result shows the micrograph of the untreated rice husk with ridged structures. The structures are punctuated with prominent domes (Luduena *et al.*, 2011; Ruseckaite *et al.*, 2007 and Park *et al.*, 2003). The silica is mainly localized in the tips of the domes, where as a lower amount of silica can be found in other regions of the rice husk. After the (NaOH + HCl) treatment, the ridged structures are broken down and the fibre surface becomes rougher. This could indicate the partial removal of silica, hemicellulose and other impurities contained in the rice husk. The (NaOH + HCl) treatment helps defibrillation and the opening of the fibre bundles. This trend increased along with the further treatment of the sample (S_2) with ($NaClO_2$ + Na_2SO_4). This indicates the partial removal of lignin and wax. The alkali treatment of the sample (S_3) with KOH indicates an increase in the separation of fibres to individual forms. The sample S_4 was submitted to acid hydrolysis in order to produce nanocellulose (NC)fibres.The (S_4) shows the distribution of the obtained nanocellulose fibres from the rice husk. It shows individual fibres which indicate that almost all the other non-cellulosic components that bind the fibril structure of the rice husk were removed. The average diameter of the nanocellulose fibres from rice husk was 8-25nm.

The micrograph clearly indicates the porous nature and rough structure of the obtained cellulose which is due to the removal of non-cellulosic component of the rice husk.The acid hydrolysis degraded the less stable amorphous segment of the obtained NC which led to the formation of cellulosic micro-sheets. The fibrils of isolated cellulose can be clearly seen from the micrograph due to the removal lignin, silica, hemicellulose and other substances from the rice husk.

However, the average diameter of the nanocellulose from rice husk was smaller than from other lignocellulosic sources such as cotton (Luduena *et al.*, 2010) and sisal (Moran *et al.*, 2008), for which the average diameter of NC fibres have been reported as 200 $\pm$ 80nm and 30.9 $\pm$ 12.5nm respectively and with smaller size distribution than NC from pineapple leaf fibre for which the diameter ranges were 5 to 60nm (Cherian *et al.*, 2010). Shukla *et al.*, (2015) produced cellulose micro sheets from rice husk using chemical method with a size ranging 180-250nm

The SEM image of the nanocellulose also shows the fibre-fibre alignment, its shape and size within the cellulose particles. It can be seen from the image that the NC has an open and fluffed up structure (with some individual strands) due to cativational milling effects on cellulosic fibres resulting out of fibre-fibre detachment.

XRD Analysis

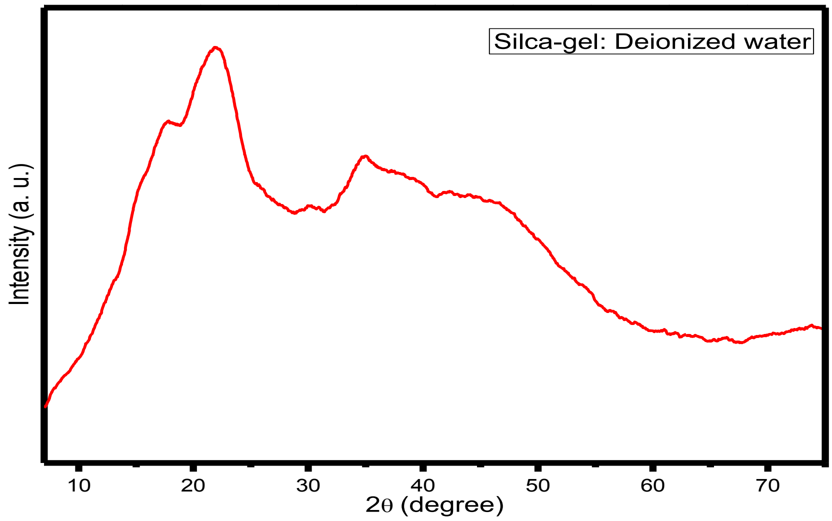

Figure 4(a): XRD of rice husk

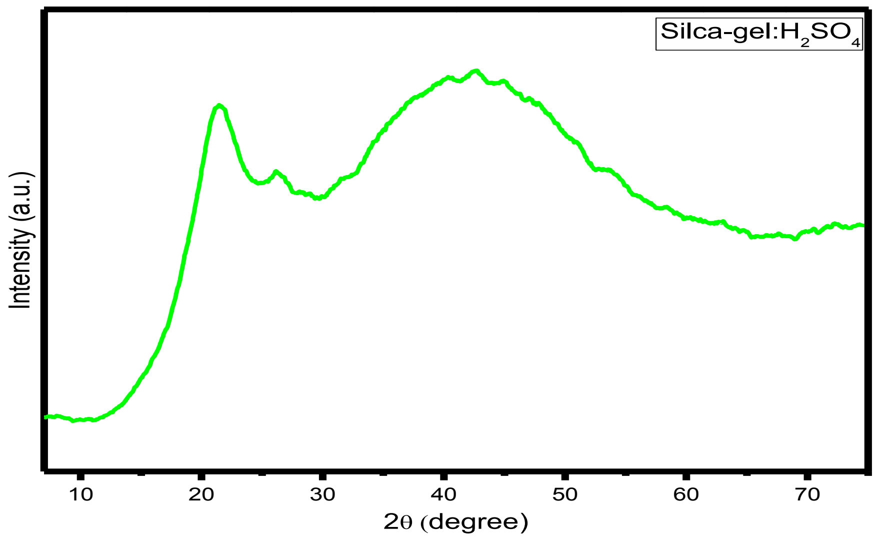

Figure 4(b): XRD of Nanocellulose

The figures 4(a and b) above show the diffractograms of rice husk and nanocellulose fibres respectively. The figure shows a broad peak between 20^0 to $30^0(2\theta)$. The removal of the non-cellulosic component of the rice husk by chemical treatment causes the change in the fibres. The alkali treatment of the natural fibres leads to the removal of cementing materials like lignin, hemicelluloses and wax.

In the study of Rezanezhad *et al.,* (2013), the nanocellulose from rice husk was obtained and the crystallinity of 71% was obtained. Luduena*et al.*, (2011) produced nanocellulose from rice husk using chemical method and the result of the X-ray diffraction showed that the crystallinity of the nanocellulose was approximately 76%. Also, Chen *et al.*, (2011) produced nanocellulose from wheat straw using mechanical method and the XRD result showed that the crystallinity of the nanocellulose was 63.4%.

However, the chemical method used to produce the nanocellulose fibres in this research work ultimately resulted in the loss of the crystalline structure of the cellulose chain. The lack of a sharp peak between 20^0 to 30^0 suggests the characteristic of amorphous cellulose.

FTIR Analysis

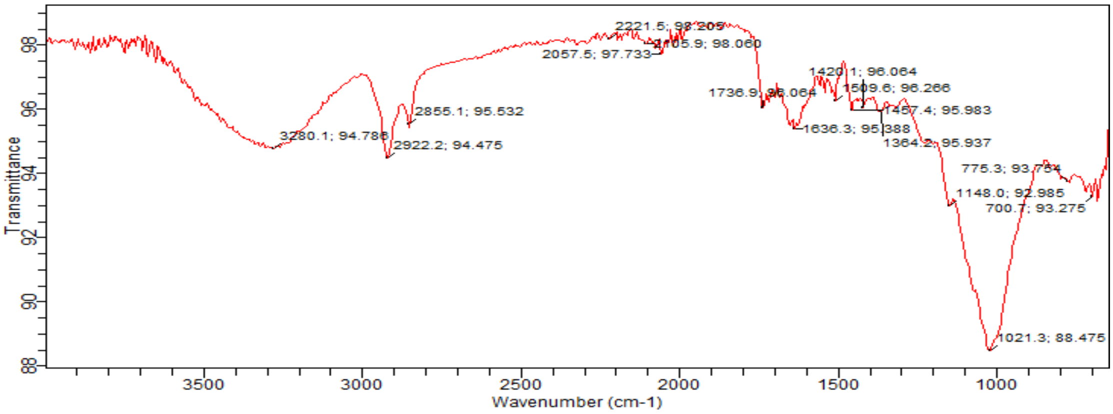

Figure 5(a): FTIR of Rice husk

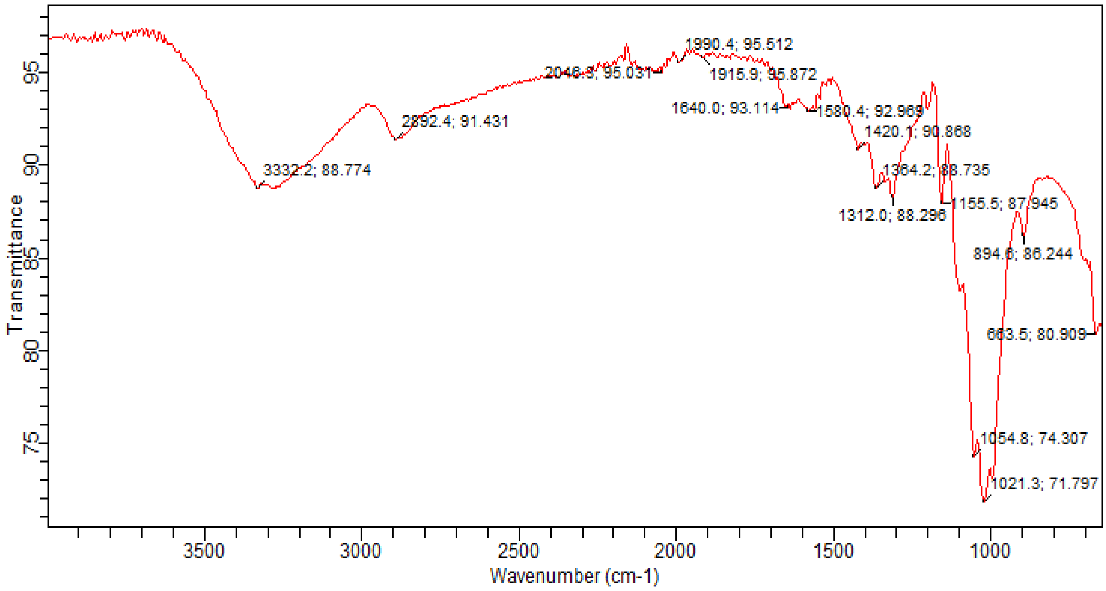

Figure 5(b): FTIR of nanocellulose

The FTIR spectral analysis of cellulose helps to understand the infrared spectral emission and changes in the molecular structure of the cellulose. The FTIR spectroscopic analysis of the nanocellulose fibres in figure 5(b) shows the changes in infrared absorption which indicates that the composition of the fibres had undergone changes during chemical treatment. The FTIR result of cellulose as compared with the previous work of Shukla *et al.*, (2015) on the extraction of cellulose micro sheets from rice husk has the following characteristics. The broad absorption peak in the range of 3600-3300cm^{-1} reveals the presence of the hydroxyl (OH) groups and the hydrophilic nature of the sample. The peak at 2916cm^{-1} may be due to the presence of the C−H stretching the vibration of the cellulose. A shoulder type of peak at around 1700cm^{-1} in the RH spectra indicates the presence of actyl or ester linkage of lignin component. This peak disappears in the spectra of the cellulose of non-cellulosic components. The peak at 1652cm^{-1}in cellulose spectra shows the presence of C=H. This peak shows the removal of hemicellulose. The peak at 1262 is due to the presence of (C-0-H aryl-alkyl). The evolution of small but sharp peak at 983cm^{-1} in the spectra of cellulose reveals its structure due the glycosidic type C−H deformation. This peak also supports the b-glycosidic linkage between the anhydroglucose units in cellulose and also indicates the change in structure of cellulose.

IV. Conclusion

Nanocellulose was successfully isolated from rice husk and has been characterized by SEM, ED-XRF, XRD and FTIR. The FTIR spectral confirmed the removal of noncellulosic components (hemicellulose, lignin, wax etc) from the extracted cellulose. The cellulose microsheet having a thickness of 8-25nm was isolated from the agrowaste.The obtained nanocelluloseshows a great potential as reinforcing filler in biodegradable nanocomposites production.

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