Journal of Chemical and Pharmaceutical Sciences ISSN: 0974-2115

Isolation of microcrystalline and nano cellulose from peanut shells

Rani Krishnan Punnadiyil*, Sreejith M. P and E. Purushothaman
Department of Chemistry, University of Calicut, Calicut University P.O., MalapuramDist, Kerala, India
***Corresponding author: Email: ranikrishnanpunnadiyil@gmail.com;Tel.: +91 9645343647**

ABSTRACT

Isolation of microcrystalline cellulose (MCC) and nano cellulose (NC) from peanut shell (PSP), which is an important agro waste has been carried out. Isolation of MCC was carried out due to its potential significance in pharmaceutical industry, using alkaline treatment followed by bleaching; and acid hydrolysis was used to isolate NC from MCC. Changes in functional groups and crystallinity of the cellulose samples during various stages of isolation were determined by FTIR and X-ray diffraction analysis respectively. FTIR spectra indicated extensive removal of hemicellulose and lignin. XRD pattern showed that the isolated MCC is crystalline in nature. The size distribution of freeze dried NC was measured by DLS. The average diameter of the NC sample has also been determined.

KEY WORDS: Peanut shell, microcrystalline cellulose, crystallinity, nano cellulose, freeze drying.

1. INTRODUCTION

India, being an agricultural country generates mind boggling amount of agricultural waste, which is over 320 million tons per year (Kim, 2004). Main sources of agro waste are paddy straw, sugar cane biogases, peanut shells, coffee husk, rice husk and maize husk. However, in our country the management of agricultural waste is very low resulting in environmental issues. By utilizing the potential benefits of these crop residues useful products can be made.

Peanuts, also known as groundnuts are an important food crop in our country with an annual production of 1.5 million tons. The peanut shell is an important agro waste with a contribution of 0.1 million tons to the total agro waste. The chemical composition of peanut shell (Raju, 2012) is cellulose (35.7%), lignin (30.2%), hemicelluloses (18.7%), and ash content (5.9%). The evaluation of luteolin from Korean peanut (Ramalingam, 2013) as well as the use of chemically modified peanut shells have been studied earlier, however, the isolation of cellulose has not yet reported. Therefore, peanut shell can be considered as a potential candidate for the isolation of cellulose.

Cellulose, being most abundant biopolymer on earth is known for its strength and stiffness. It is important natural filler owing to its renewable and biodegradable nature and its annual production is estimated to be 7.5×10^{10} tons (French, 2004). The hydrogen bonding ability of the three hydroxyl groups present in the structure of cellulose are responsible for the varied applications of cellulose due to enhanced physical and mechanical properties (John, 2008). Cellulose (mainly freeze dried NC) finds potential application in pharmaceutical chemistry (Kamel, 2008) due to its biocompatibility and biodegradability. The development of cellulose based biomedical scaffolds has gained attention in recent times. The process of extraction of cellulose utilizes the removal of hemicellulose and lignin which constitutes the matrix for cellulose micro fibrils. The isolation and characterization of cellulose from different sources like corn stalk (Reddy et al. 2005), rice husk (Reddy and Yang, 2005), sugar cane bagasse (Sun, 2005), coconut husk (Rosa, 2010), wood (Orts, 2005) etc. have been previously reported. However, the isolation of cellulose from an easily available, abundant source, which is regarded as a waste; peanut shell has not been reported so far. Therefore, the main objective of this investigation is to isolate and characterize cellulose from peanut shell.

2. EXPERIMENTAL

2.1. Materials: Peanut shells obtained from a local mill near Palakkad were used as the raw material. Chemicals used were NaOH (Merck), NaOCl, HNO_3 and Ethanol. All chemical used for the isolation are of reagent grade.

2.2. Isolation of MCC: The peanut shells were washed with running water and sundried for three days to remove moisture. Dried shells were then ground into powder form using a mill, and were sieved using 90µm mesh. 25 g of the powder was treated with NaOH (750 ml, 0.5M) for 2 hours at 95^0C with continuous stirring. The dark slurry obtained was filtered and washed several times with distilled water and then dried.

The dried powder was refluxed with a mixture containing 20% (v/v) of nitric acid in ethanol. This treatment was carried out thrice and the colour changed from brown to yellow in successive steps. The mixture was then filtered and washed with cold distilled water till the solution becomes neutral. The yellow coloured residue was then bleached with sodium hypochlorite to get off-white cellulose. It was then oven dried over night at 60^0C to constant weight. Finally, the dried cellulose was ground and kept in polyethylene bags. The total yield of extracted cellulose was 32 wt %. Photographs at different stages of chemical treatments are shown in Figure 1.

a b c d

Fig.1. Photographs of (a) pure PSP (b) alkali treated (c) HNO_3/ ethanol refluxed (d) MCC

2.3. Preparation of Nano Cellulose from MCC by Acid hydrolysis: About 5g of MCC (isolated from peanut shell) was mixed with sulphuric acid (64 wt%, 45 ml) kept in an ice bath, the mixture was stirred for 120 min at 45^0C using a magnetic stirrer. About 500 ml of water was added to the reaction mixture to quench hydrolysis and then washed till the solution became neutral. The resultant suspension was kept for freeze-drying. Photograph of NC suspension is shown in Figure 2.

Fig.2. Photograph of NC suspension

2.4. Characterization: FTIR was carried out by using JASCO FTIR-4100 spectrometer using KBr pellet. IR spectra were recorded in the range of 4000-400 cm^{-1}. Crystalline nature of isolated MCC was measured using RIGAKU MINIFLEX-600 diffractometer with Cu Kα (λ=1.54 A^0) with scanning in a 2θ range of 10^0 to 50^0, and a step size of 0.02^0. The size distribution and mean diameter particle size of freeze dried NC were estimated by Dynamic Light Scattering (DLS) using a Zetasizer Nano ZS instrument (Malvern). Measurements were performed at an angle of 170^0 using a He-Ne laser operated at 633 nm, on diluted sample.

3. RESULTS AND DISCUSSION

3.1. FTIR analysis: FTIR spectra of untreated PSP, alkali treated, ethanol refluxed and MCC are presented in Figure 3. Difference in intensities of FTIR bands showed that changes have occured during chemical treatment (Sun, 2004). All the spectra has broad band in the region of 3400 cm^{-1}, 2900 cm^{-1} and 1627 cm^{-1}. The one at 3400 cm^{-1} corresponds to the free O-H stretching vibration of OH group in cellulose. Those at 2900 cm^{-1} and1627 cm^{-1}were assigned to C-H stretching vibration (Abdul Khalil et al. 2001) and O-H bending of absorbed water (Troedec, 2008).

Pure PSP showed strong absorption frequency at 1735 cm^{-1} and 1247 cm^{-1} (Oh, 2005), corresponding to C=O stretching vibration of acetyl group from lignin and hemicelluloses; and C-O out of plane stretching vibration of phenyl group in lignin. These two bands gradually disappeared during chemical treatment. The absence of these two bands in MCC indicates the complete removal of lignin and hemicelluloses (Viera, 2007).

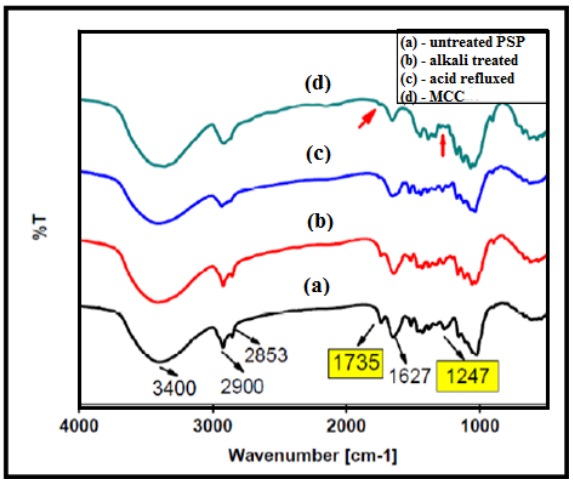

Fig.3. FTIR spectraof (a) untreated PSP (b) alkali treated (c) acid refluxed (d) MCC

3.2. XRD analysis: Figure 4 shows the X-ray diffraction pattern of untreated PSP and those at different stages of chemical treatments. PSP exhibited a broad peak at $2\theta = 22.6^0$, which indicates the presence of amorphous material (Subramanian et al. 2005) and small less prominent peaks at $2\theta = 16^0$ and 35^0. The peak at $2\theta = 22.6^0$ becomes more prominent and sharper as it reached MCC after various chemical treatments. This gave an insight on to the crystalline nature of MCC.

The crystallinity index and crystallite size for untreated PSP, alkali treated, ethanol/HNO_3 refluxed and MCC were calculated using eq. 1 (Bansal et al. 2010) and 2, and the results are represented in Table 1.

$$CrI\ (\%) = [(I_{(002)} - I_{(am)})/ I_{(002)}] \times 100 \qquad (1)$$

Where CrI is the crystalline index, I_{002} is the maximum intensity of the (002) lattice diffraction and the I_{am} is the intensity diffraction at 16^0, 2θ degrees.

$$D_{(hkl)} = K\lambda/\beta_0 \cos\theta \qquad (2)$$

Where $D_{(hkl)}$ is the crystallite size (nm), K is the Scherrer constant (0.94), and λ is the X-ray wavelength (0.15418 nm for Cu). β_0 is the full-width half-maximum of the reflection hkl, and 2θ is the corresponding Bragg angle.Results show that crystallinity has increased two folds for MCC than PSP, and this is attributed to the removal of amorphous constituents along with lignin and hemicelluloses. Furthermore, crystallite size has decreased for MCC when compared to untreated PSP.

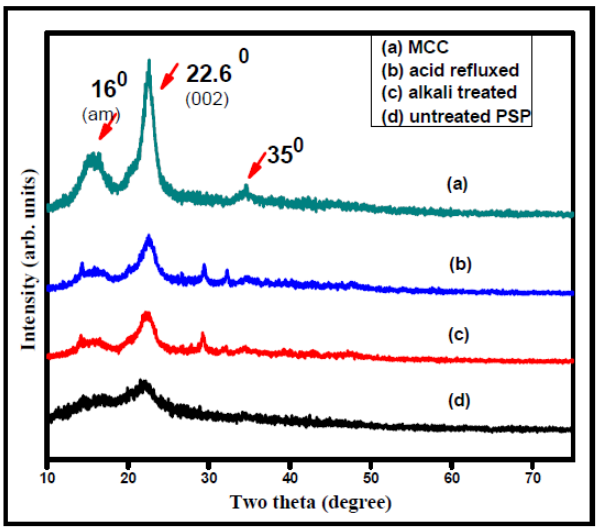

Figure.4. XRD patterns of (a) MCC (b) acid refluxed (c) alkali treated (d) untreated PSP

Table.1.Crystalline characteristics of PSP at different stages

Fiber Stage	Crystallinity Index (CI) %	Crystallite Size (nm)
Untreated PSP	26.5	5.1
Alkali-treated	57.3	3
Ethanol/HNO_3 refluxed	63.4	3.4
MCC	66.4	1.6

3.3. DLS analysis: The average particle size and particle size distribution of freeze-dried cellulose samples were measured using DLS. Size distribution graph is shown in Figure 5. Table 2 shows DLS data of freeze-dried sample obtained by acid hydrolysis. The average particle size obtained is 343 nm showing the nano nature of the cellulose sample derived as a result of acid hydrolysis from the MCC. Almost 99.9 % of the sample showing particle range in between 100 – 1000 nm, showing the presence of only one class of compound.

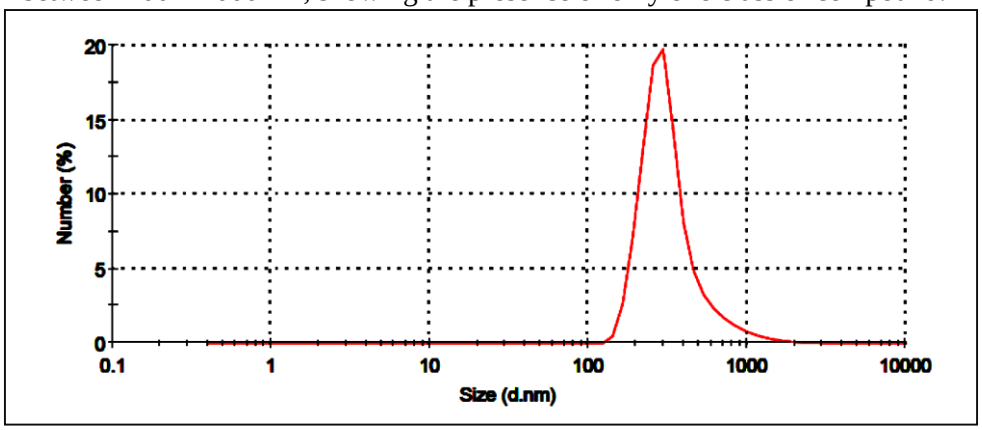

Fig.5. Size distribution of freeze dried cellulose samples by number

Table 2.DLS data of freeze-dried sample obtained by acid hydrolysis

Peak No.	Size (d.nm)	Number (%)
1	343.3	99.9
2	4578	0.1

4. CONCLUSIONS

MCC, an important constituent in pharmaceutical industry was isolated from PSP which is an agro waste by alkaline treatment followed by bleaching. NC was prepared successfully by acid hydrolysis of derived MCC. FTIR spectra confirmed the removal of hemicelluloses and lignin, which proves the isolation of MCC from PSP. XRD pattern showed that the crystallinity has increased for MCC, this confirms the removal of some of the amorphous parts from PSP during various stages of chemical treatment. The isolation of NC was successfully carried out by acid hydrolysis of MCC. The particle size distribution resulted in one peak with 99.9 % of particles around 343 nm.

5. ACKNOWLEDGEMENTS

The authors thank the UGC, New Delhi for financial support and the Department of Chemistry, University of Calicut for facilities.

REFERENCES

Abdul Khalil HPS, Ismail H, Rozman HD, and Ahmad M N, The effect of acetylation on interfacial shear strength between plant fibres and various matrices, J. Eur. Polym., 37, 2001, 1037-1045.

Bansal P, Hall M, Realff MJ, Lee JH, Bommarius AS, Multivariate statistical analysis of X-ray data from cellulose: A new method to determine degree of crystallinity and predict hydrolysis rates, Bio resour. Technol., 101, 2010, 4461-4471.

French AD, Bertoniere NR, Brown RM, Chanzy H, Gray D, Hattori K, Glaasser W, In Kirk-Othmer Encyclopedia of Chemical Technology, 5th ed., 5, 2004.

John MJ, and Thomas S, Bio fibres and bio composites, Carbohydr. Polym., 71, 2008, 343.

Kamel S, Ali N, Jahangir K, Shah SM, El-Gendy AA, Pharmaceutical significance of cellulose: A review, Express Polymer Letters, 2, 2008, 758–778.

Kim S, Dale BE, Global potential bioethanol production from wasted crops and crop residues, Bio mass and Bio energy, 26, 2004, 361-375.

Oh SY, Yoo DI, Shin Y, Seo G, FTIR analysis of cellulose treated with sodium hydroxide and carbon dioxide, Carbohyd. Res., 340, 2004, 417-428.

Orts WJ, Shey J, Imam SH, Glenn GM, Guttman ME, Application of Cellulose Microfibrils in Polymer Nano composites, Revol. J. Polym. Envir., 13,2005, 301-306.

Raju GU, Kumarappa S, Gaitonde VN, J.Mechanical and physical characterization of agricultural waste reinforced polymer composites, Mater. Environ. Sci., 3, 2012, 907-916.

Ramalingam R, Suk-Bok P, Byoung-Kyu L, In-Youl B, Evaluation of luteolin from shells of Korean peanut cultivars for industrial utilization, Afri. J. Biotech., 12, 2013, 4477-4480.

Reddy N, Yang Y, Properties and potential applications of natural cellulose fibers from cornhusks, Green Chem., 7, 2005, 190-195.

Reddy N, Yang Y, Structure and properties of high quality natural cellulose fibers from cornstalks, Polymer, 46, 2005, 5494-5500.

Rosa MF, Medeiros ES, Malmonge JA, Gregorski KS, Wood DF, Mattoso LHC, Glenn G, Orts WJ, Imam SH, Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior, Carbohydr. Polym., 81, 2010, 83-92.

Troedec M, Sedan D, Peyratout C, Bonnet J, Smith A, Guinebretiere R, Influence of various chemical treatments on the composition and structure of hemp fibres, Composites Part A – Applied Science and Manufacturing, 39, 2008, 514-522

Viera RGP, Rodrigues G, Assuncao RMN, Meireles CS, Vieira J, Oliveira GS, Synthesis and characterization of methylcellulose from sugar cane bagasse cellulose. Carbohydr. Polym., 67, 2007, 182–189.