Obtaining cellulose from Cotton Stalk, microcrystalline cellulose, and cellulose aerogel, and study of their properties

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Abstract. In the process of extracting cellulose from rice stems using the sodium method, the effect of the alkali solution concentration was studied and microcrystalline cellulose was synthesized from the obtained cellulose. Structural and morphological characteristics of rice cellulose fibers were studied. The average length and width of cellulose fibers, their fractional composition and shape factor were determined on an automatic Fiber Tester analyzer. The structure of the obtained cellulose and MCS was determined by X-ray diffraction, IR spectroscopy, adsorption isotherm on a McBen-Bakr device, saturated adsorption of polar and non-polar molecules. The influence of the synthesis time of cellulose from rice stems and MCS from the obtained cellulose on the physicochemical properties was studied. MCC yield best at 45 min hydrolysis Aerogel was extremely porous, crystallinity reduced after processing, successful synthesis of MCC and aerogel, properties confirmed by XRD, IR, adsorption and promising for industrial use

1 Introduction

Significant attention is being paid worldwide to the synthesis of cellulose and its alkyl-, acyl-, and alkoxy-derivatives from annual plant stems, as well as to the study of their physicochemical and performance properties. Scientific research in this area is particularly focused on developing biologically pure fillers and binders, using these materials as antioxidants, creating compositions with improved technical and specific characteristics, and developing technologies for the production of microcrystalline cellulose (MCC) from unconventional sources [1].

One of the research directions in cellulose science is its physical modification. Through physicochemical methods specifically thermochemical treatment the dimensions and fibrillation degree of cellulose fibers are altered.

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When such modified cellulose is used as a raw material, the resulting products exhibit enhanced physical and mechanical properties. When the fiber size is drastically reduced to the nano scale, it can serve as functional filler in various composite materials [2].

Our objective is to develop a method for synthesizing microcrystalline cellulose (MCC) from rice straw and to investigate its comprehensive properties, as well as to elaborate a technology for obtaining aerogels from this cellulose [3].

2 Methods

Rice straw cellulose was subjected to deep hydrolysis using thermo-mechanical methods to achieve a micro-sized structure. The characteristics of the fibers were measured using a modern automated Fiber Tester [1], which determines the fractional composition of the fibers.

Physicochemical properties were analyzed using modern instruments, including X-ray diffraction (XRD), IR spectroscopy, microscopy, and adsorption isotherm analysis using the Mac-Ben-Bakra vacuum apparatus. The structural characteristics of the fibers were also examined in detail.

3 Results and Discussion

Cellulose was synthesized from rice straw. A total of 400 grams of rice straw was loaded into an autoclave. Alkaline solutions with concentrations of 2%, 4%, 6%, 8%, and 10% were prepared. The autoclave was charged with 400 g of rice straw and treated with 4% NaOH solution at a material-to-liquor ratio of 1:10.

Cooking durations were set at 1, 2, 3, 4, 5, and 6 hours, under a pressure of 0.3–0.4 MPa at 135–140°C. A brief characterization of the results obtained is presented in Table 1.

Table 1. The influence time on rice straw cooking

Time (hr)	NaOH, %	Yield, %	Water absorption capacity, %	Ash content, %
1	4	60.2	125	12.1
2		58.0	140	12.8
3		55.6	180	13.6
4		46.8	226	14.1
5		45.6	225	14.0
6		45.0	225	14.0

As the cooking time increased, the yield of the obtained semi-finished cellulose gradually decreased. That is, after 1 hour of cooking, approximately 40% of polysaccharides were dissolved and transferred into the solution. With longer cooking durations, the yield continued to decline.

After 6 hours of processing, the yield of the product decreased to 45%. Other indicators such as water absorption capacity (ranging from 125% to 225%) and ash content (ranging from 12.1% to 14.0%) showed an increasing trend.

The influence of alkali solution concentration on the cooking process was studied. Table 2 provides a brief characterization of the obtained results.

Table 2. The influence of alkali concentration on rice straw cooking (duration: 4 hours)

NaOH, %	Time, hour	Yield, %	Water absorption capacity, %	Ash content, %
1	4	61.1	121	14.3
2		54.5	145	14.1
3		51.6	181	14.2
4		46.8	226	14.1
5		45.8	224	13.2
6		46.1	224	13.2

As the alkali concentration increased during the cooking process, the yield of the semi-finished cellulose product gradually decreased. For instance, when cooked in a 1% alkali solution, approximately 39% of polysaccharides dissolved and transferred into the liquor. With increasing alkali concentration, the overall yield continued to decline. However, at a 6% alkali concentration, the yield of the final product reached 46.1%.

The characteristics of the rice-based cellulose obtained under optimal process conditions were compared with those of "Armicel" produced in the Russian Federation. The comparative results are presented in Table 3.

Table 3. Characteristics of rice straw cellulose and "Armicel" cellulose fibers

No.	Name of indicators	Indicators value	
		Rice straw cellulose fibers	"Armcel" cellulose fibers
1.	Appearance	White fibers with foreign inclusions	White fibers with foreign inclusions
2.	Bulk density, kg/m^3	100-150	100-150
3.	Moisture content, max (%)	7	8
4.	Solubility	Insoluble in water and organic solvents	Insoluble in water and organic solvents
5.	Fiber length, mm	From 0.2 – 0.5 to 5.5 - 6	From 100 to 2000
6.	Fiber diameter, mm	0.1376	Maximum 35
7.	Water ion concentration (pH)	6 – 7.5	6 – 7.5
8.	Thermal resistance, at 220^{o}C, mass loss, %	-	7

3.1 Synthesis of Purified Cellulose

A pre-prepared 4% NaOH solution (4000 mL, module 1:10) was poured and heated. Within 15 minutes, the temperature of the mass inside the autoclave reached 135°C under a pressure of 0.35 MPa, and the cooking process continued under these conditions for 4 hours. After cooling for 60 minutes, the mass was removed from the autoclave and washed to a neutral pH (the mass appeared black in color). Subsequently, the wet hemicellulose mass was disintegrated in a disintegrator and bleached using a 3% hydrogen peroxide solution. It was then washed to neutral pH and dried at room temperature to obtain purified cellulose.

3.2 Synthesis of Microcrystalline Cellulose

The synthesis of microcrystalline cellulose (MCC) was carried out under laboratory conditions in a round-bottom flask. Around 200 g of air-dried rice cellulose (hereafter referred to as RC) was weighed and placed into a 3-liter round-bottom glass flask. A hydrolyzing mixture composed of 2 L of 3% H_2SO_4 and 3% N_2O_2 solutions in a 1:1 ratio was added [2]. MCC samples obtained after 15, 30, 45, and 60 minutes of hydrolysis were analyzed for their physicochemical properties, which are presented in Table 4.

As seen from the table, the sorption capacity of MCC is highest when the hydrolysis duration is 45 minutes (with atmospheric moisture absorption at 12.3% and water absorption capacity at 254%). The bulk density of the MCC is low—0.29 g/cm³—while the porosity is high, reaching 75%.

Table 4. The influence of synthesis time on the physicochemical properties of MCC obtained from rice straw cellulose

Hydrolysis time, min	Moisture absorption from air,%	Water absorption capacity,%	Bulk density, g/cm^3	Ash content,%	Porosity, %
15	12.0	246	0.49	14.8	68
30	12.1	253	0.42	14.3	73
45	12.3	254	0.29	14.2	75
60	13.4	258	0.39	14.6	76
90	13.4	259	0.40	14.6	76

The mass is then boiled for 60 minutes. Afterward, the reaction mixture is washed to a neutral pH, and the microcrystalline cellulose is separated by filtration. The wet MCC is thinly spread onto a polyethylene film and dried at room temperature for 24 hours. Once the moisture content of the obtained MCC is determined, its yield is calculated as a percentage relative to the dry weight of the initial rice straw.

The structural characteristics of the aerogel synthesized from microcrystalline cellulose are presented in Table 5.

Table 5. Structural characteristics of MCC Aerogel

Bulk density of aerogel, r_{bulk}, g/cm^3	Pure cellulose density, $r_{pure,}$ g/cm^3	Porosity , P, %
0.056	1.54	96.3

The porosity of the aerogel sample was found to be very high by reaching 96.3%. The structural and morphological characteristics of rice straw cellulose fibers were studied. The average length, width, fractional composition, and shape factor of rice cellulose fibers were determined using the Fiber Tester automatic analyzer. The lengths of rice cellulose fibers were found to vary widely, ranging from 100–110 microns up to 140–10,000 microns (Figures 1–3).

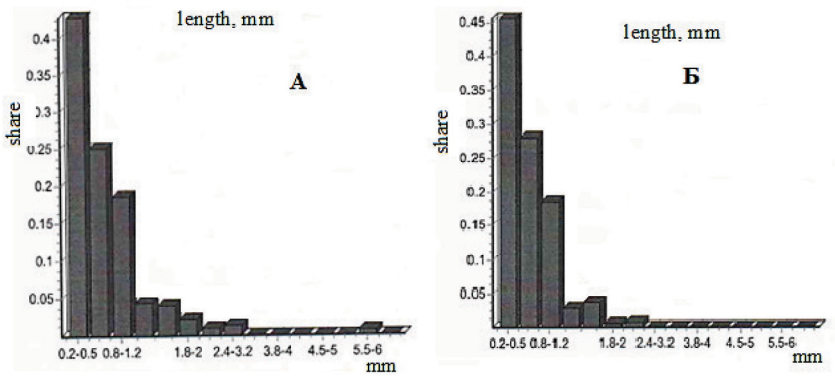

Fig. 1. Average fractional composition by fiber length: A – Cellulose; B – MCC.

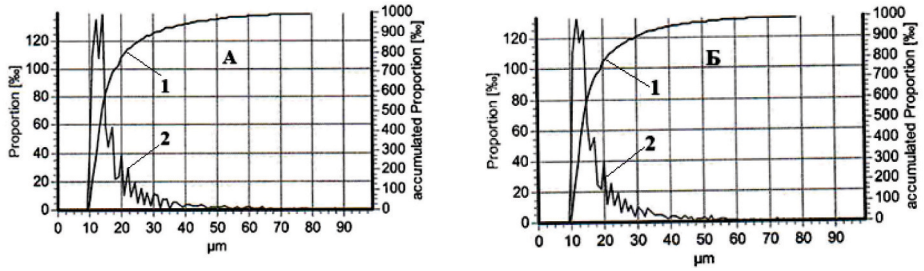

Fig. 2. Integral (1) and differential (2) with respect to the length of the fibers: A – Cellulose; B – MCC.

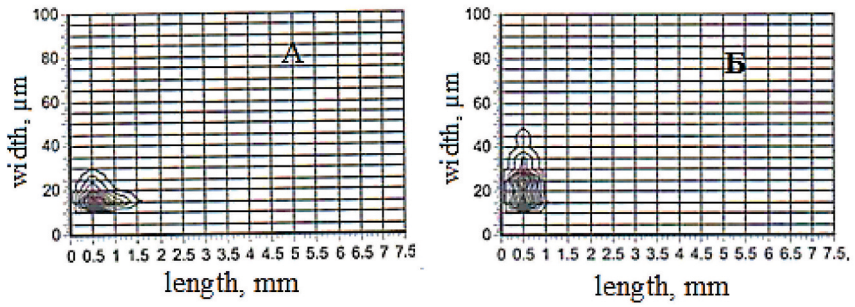

Fig. 3. Average fiber shape factor: A – Cellulose; B – MCC.

Tables 6 and 7 provide detailed data on the fiber dimensional distribution. The cellulose fibers were divided into four groups based on their sizes: 0.10–0.20 mm; 0.20–0.30 mm; 0.30–0.40 mm; and 0.40–10.00 mm. Table 6 shows the average fractional composition of cellulose fibers, while Table 7 presents the average fractional composition of microcrystalline cellulose (MCC) fibers.

According to the results obtained from the Fiber Tester apparatus, the analysis of 3599 cellulose fibers yielded an average fiber length of 0.8422 mm and an average width of 0.1376 mm. This means that the average fiber width is approximately 6.12 times shorter than the fiber length.

The average length and width of 3,562 microcrystalline cellulose fibers measured using the Fiber Tester device were found to be 0.2230 mm and 0.1169 mm, respectively. Thus, the average width of the fibers is approximately 1.90 times shorter than their length.

Table 6. Average fractional composition of cellulose fibers

mμ \ Mm	0.10 – 0.20	0.20 – 0.30	0.30 – 0.40	0.40 – 10.00
100-110	0.0	2.0	0.9	33.5
110-120	0.0	1.0	0.5	6.3
120-130	0.5	0.7	0.5	5.5
130-140	0.3	0.9	1.3	7.8
140-10000	3.0	3.3	0.0	32.1
mμ \ 100%	**3.8**	**7.9**	**3.2**	**85.1**

Table 7. Average fractional composition of microcrystal cellulose fibers

mμ \ mm	0.10 – 0.20	0.20 – 0.30	0.30 – 0.40	0.40 – 10.00
100-110	0.0	0.0	0.0	0.0
110-120	41.1	58.9	0.0	0.0
120-130	0.0	0.0	0.0	0.0
130-140	0.0	0.0	0.0	0.0
140-10000	0.0	0.0	0.0	0.0
mμ \ 100%	**41.1**	**58.9**	**0**	**0**

3.3 X-ray Structural Analysis

The crystallinity degree of cellulose and microcrystalline cellulose samples was determined using the D2 PHASER (Bruker) X-ray diffractometer. Initially, the samples were pressed into tablet form, and corresponding X-ray diffraction patterns were recorded. The crystallinity index was then calculated using standard methods. To evaluate the crystallinity degree of the cellulose-based aerogel sample, test specimens with dimensions of 35 mm in diameter and 1.0–1.2 mm in height were prepared.

The measurements were carried out on an “Empyrean PANalytical” X-ray diffractometer using a filtered copper anode. As stated in patent US 5769934, various physicochemical treatments applied to natural cellulose decrease its crystallinity and lead to a transformation into nano-sized cellulose of type II. These structural changes are confirmed by the results of X-ray diffraction (XRD) analysis (Figure 4).

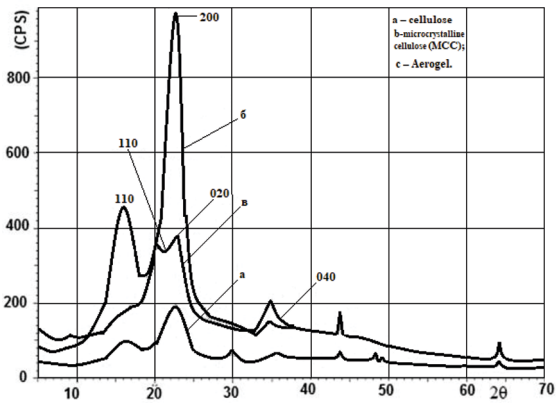

Fig. 4. Diffractograms of the samples: a – cellulose; b – microcrystalline cellulose (MCC); c – Aerogel.

The figure presents the diffractograms of cellulose, microcrystalline cellulose, and aerogel samples obtained from rice straw.

The X-ray diffractograms of the samples exhibit distinct diffraction peaks:

Figure 3.7 – Diffraction Peak Positions: a) Cellulose: Maximum 2θ diffraction angles observed at: 2θ = 16.4°, **23.5°,** 30.0°, 35.0°, 40.0°, 43.0°, 48.0°, and 63.5°; specific crystallographic planes: 110, 200, 040. b) Microcrystalline Cellulose (MCC): Maximum 2θ angles at: 2θ = 16.0°, **23.0°,** 35.0°, 43.8°, and 64.0°; specific crystallographic planes: 110, 200, 040. c) Aerogel: Maximum 2θ angles at: 2θ = 16.8°, **20.5°**, 24.8°, 30.0°, 33.5°, 34.5°, and 64.0° specific crystallographic planes: 110, 200, 020, 040.

Table 8. Crystallinity degree of cellulose, MCC, and aerogel obtained from rice straw

Sample	**X-ray diffraction intensity at 2θ° for the 200 plane**	**Crystallinity degree (%)**
Cellulose	23.5	63,1
Microcrystalline cellulose	23.0	73
Aerogel	20.5	55.

In the 200 plane, the angle 2θ of cellulose and MCC is close to each other. In aerogel, a significant decrease in the intensity reflex is observed at angles 2θ: 2θ,5°. The reason is that the results of chemical and mechanical processing of cellulose partially damage its ordered crystalline structure. According to the analysis of X-ray diffraction patterns, the degree of crystallinity of rice cellulose was 63.1; MKS - 73; the lowest is for aerogel - 55. The low crystallinity of aerogel is due to the mechanochemical and ultra-low-temperature processing of its production technology.

3.4 Infrared spectroscopy

The IR spectroscopic research method determines the chemical changes in the sample. The IR-Fourier spectrometer was obtained on a "SHIMADZU" (Japan) spectrophotometer. Range 400-4000 cm^{-1}, detection limit 4 cm^{-1}. The spectra were obtained by pressing KBr (2 g of KBr and 9 mg of sample). The average error in this case is +5%. In the spectra, we focused on the difference between the cellulose sample in the range of 4000 - 2000 cm^{-1}.

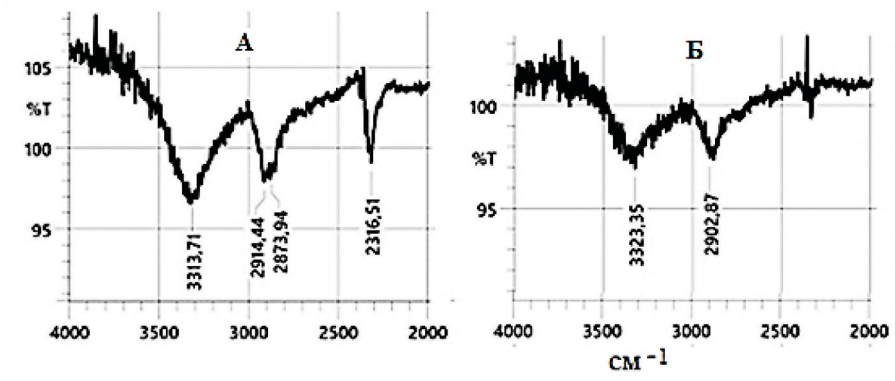

Fig. 5. IR-spectrum of MKS of rice straw (A) and aerogel obtained from it (B).

In the IR spectrum of microcrystalline cellulose synthesized from rice straw cellulose and aerogel obtained from it, the vibration frequencies correspond to 3500-3000 cm^{-1}, the valence vibration is wide and intense. That is, cellulose participates in forming hydrogen

bonds between molecules. Absorption regions 2914, 44; The correspondence of 2873.94 (MKS) and 2902.87 (aerogel cellulose) cm^{-1} indicates the presence of CH_2. These frequencies are usually used as an internal standard. In microcrystalline cellulose, there is an absorption band of 2316.51 cm^{-1}, and in aerogel cellulose, it is not noticeable, has a valence bond, medium intensity. The difference between the IR-spectra of the two samples is very small.

3.5 Optical Microscopy

Optical microscopy was used to study the morphology of cellulose fibers. The external appearance of cellulose fibers isolated from rice straw is presented at magnifications ranging from 40x to 400x (Fig. 6). Their dimensions and appearance after alkaline hydrolysis are also shown. The fiber lengths vary, and since they were obtained in the laboratory, they are not fibrillated.

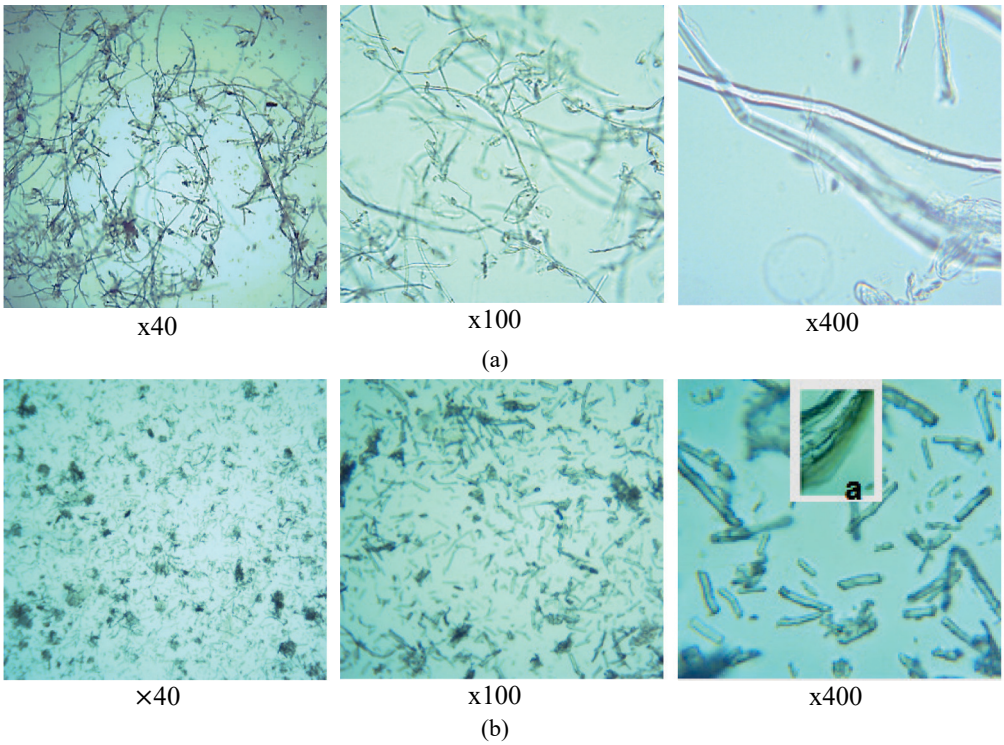

Fig. 6. Microscopic magnification of (a) rice straw cellulose and, (b) MCC fibers at a magnification of 40-400 times

In enterprises, fiber fibrillation is carried out in special fibrillating working bodies of the roll apparatus. A microphotograph of microcrystalline cellulose fibers is presented in Fig. 6. After the MKS was synthesized, it was first crushed in a laboratory roll apparatus, then, additional processing was carried out in a refiner that made the fibers uniformly long. Fibrillation of the fibers is not visible when magnified 40 and 100 times, but fibrillated parts of some fibers are visible when magnified 400 times.

3.6 Measurement of adsorption isotherms using the Mac-Ben-Bakr vacuum balance apparatus

As noted in sources [6,7], vapor adsorption isotherms on porous sorbents can be determined using a gravimetric method. The measurement is carried out on a high-vacuum apparatus known as the Mac-Ben-Bakr balance, which utilizes a quartz spring. The essence of the method lies in suspending a cup containing the adsorbent sample on a quartz spring; as adsorption occurs, the spiral spring extends, and the quantity of adsorbed substance is determined based on the deformation of the spring. The elongation of the spring is measured with an accuracy of approximately 0.01 mm using a KM-9 cathetometer.

Adsorbent samples (rice straw cellulose, microcrystalline cellulose synthesized from it, and MCC aerogel) were weighed at 1.0 g using an analytical balance and placed under vacuum using VN–461M fore-vacuum and diffusion pumps until a residual pressure of 1.33 × 10^3 Pa was achieved. The pressure in the system was monitored using a VIT–2 thermovacuum gauge. A vacuum level of 1–10^{-5} mm.s.ust. was established in the adsorption system using the fore-vacuum and diffusion pumps.

From the data obtained, it can be observed that the adsorption isotherms of rice cellulose and its derived MCC samples are nearly identical up to a relative pressure (r/r_s) of 0.4. However, beyond this point, as the relative pressure increases from 0.4 to 1.0, the monolayer capacity of the adsorbents increases significantly. After r/r_s surpasses 1.0, a clear difference in adsorption capacity is observed between the samples, ranging from 1.4 to 2.5 mole/kg, as shown in Fig. 7.

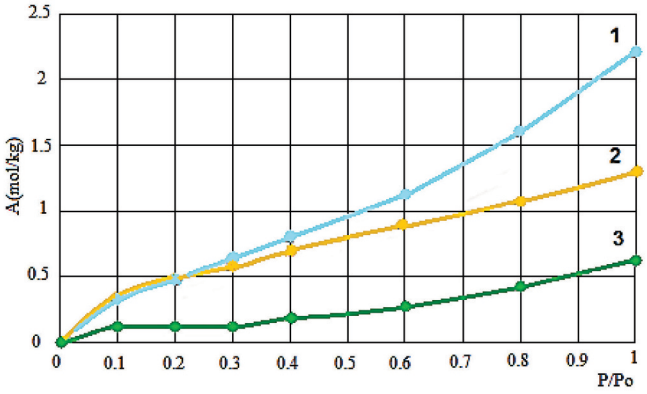

Fig. 7. Adsorption isotherm obtained from the sample: 1 – cellulose aerogel; 2 – cellulose; 3 – MCC.

In cellulose aerogel, the monolayer capacity increases uniformly and reaches 0.7 mol/kg. The adsorption of the obtained samples by water vapor, which is considered a polar molecule, was also studied (Tables 9-11).

The results are presented in Table 9 below, based on the benzene and water vapor isotherm data, and the sorption-structure properties and pore sizes of the adsorbent microcrystalline cellulose and cellulose aerogel particles. The results show that the adsorption of benzene and water vapor increases with the size of the mesoporous pores.

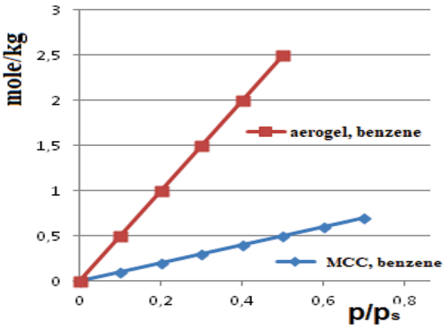

Fig. 8. Sorption of benzene vapor by rice aerogel and rice MCC.

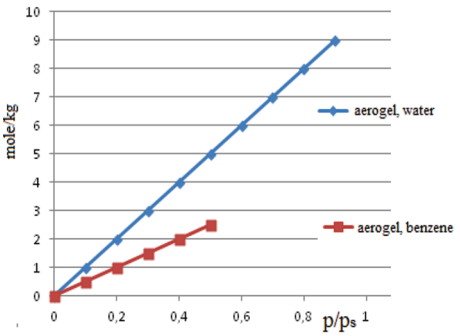

Fig. 9. Sorption of water vapor and benzene vapor by rice aerogel.

Table 9. Benzene and water vapor adsorption of rice cellulose

No.	Name	Benzene	Water
		Amount	Amount
1	a_m, monolayer capacity, mole/kg	0.402	2.116
2	S, comparative surface, m^2/g	96.82	137.59
3	W_o, micropore size, $W_o \cdot 10^3$, m^3/kg	0.0858049	0.116432
4	V_s, saturation volume, $V_s \cdot 10^3$, m^3/kg	0.1146068	0.166086
5	W_{me}, mesopores size, $W_{me} \cdot 10^3$, m^3/kg	0.03	0.05
6	Pore radius, Å (nm)	23.7 (2.37)	24.1(2.41)

Table 10. Benzene and water vapor adsorption of rice straws

No.	Name	Benzene	Water
		Amount	Amount
1	a_m, monolayer capacity, mole/kg	0.093	1.439
2	S, comparative surface, m^2/g	22.49	93.59
3	W_o, micropore size, $W_o \cdot 10^3$, m^3/kg	0.0276447	0.0703352
4	V_s, saturation volume, $V_s \cdot 10^3$, m^3/kg	0.0551318	0.103446
5	W_{me}, mesopores size,, $W_{me} \cdot 10^3$, m^3/kg	0.03	0.03
6	Pore radius, Å (nm)	49.0 (0.49)	22.1(2.21)

Table 11. Adsorption of benzene and water vapor by rice cellulose aerogel

No.	Name	Benzene	Water
		Amount	Amount
1	a_m, monolayer capacity, mole/kg	0.346	1.733
2	S, comparative surface, m^2/g	83.36	112.66
3	W_o, micropore size, $W_o \cdot 10^3$, m^3/kg	0.0972998	0.0910275
4	V_s, saturation volume, $V_s \cdot 10^3$, m^3/kg	0.16185	0.142218
5	W_{me}, mesopores size,, $W_{me} \cdot 10^3$, m^3/kg	0.06	0.05
6	Pore radius, Å (nm)	38.8 (3.88)	25.2(2.52)

4 Conclusion

Microcrystalline cellulose was synthesized from rice cellulose. The structures of rice cellulose and MCC were studied. The micro and meso pores of rice cellulose and rice MCC samples were studied for polar water vapor and non-polar benzene vapor adsorption using

the Mac-Ben-Bakra device. The structures of rice cellulose and MCC were studied. MCC yield best at 45 min hydrolysis Aerogel was extremely porous, crystallinity reduced after processing, successful synthesis of MCC and aerogel, properties confirmed by XRD, IR, adsorption and romising for industrial use.

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