Chemistry, Physics and Technology of Surface. 2024. V. 15. N 1. P. 57-66

UDC 676.16.022.6.031+576.166.3+544.032.72 doi: 10.15407/hftp15.01.057

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PHYSICO-CHEMICAL CHARACTERISTICS OF MICROCRYSTALLINE CELLULOSE FROM SWITCHGRASS *(Panicum virgatum L.)* OBTAINED IN THE PRESENCE OF A SOLID CATALYST

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The main idea of this work is the investigation of structural and morphological characteristics of microcrystalline cellulose with switchgrass (Panicum virgatum L.) by the method of organo-solvent cooking with the addition of various brands of ion-exchange resins instead of sulfuric acid. A sulfonated copolymer of styrene and divinyl benzene with two functional groups per ring - Purolite CT-275 and a sulfonated copolymer based on tetrafluoroethylene - Nafion NR-50 were chosen as initial ion exchange resins. Air-dry switchgrass (Panicum virgatum L.), a technical culture, was used for the research. Microcrystalline cellulose (MCC) was obtained from it by the method of organo-solvent cooking with the addition of a solid catalyst. Using the methods of XRD, FTIR-ATR, AFM, TGA and DSC, the structure and morphology of MCC were studied. It is found that the use of ion-exchange resins in the organo-solvent method of obtaining MCC in a batch reactor requires the use of protective covers for the catalyst to avoid its mechanical damage. It has been found that only sulfonated copolymers based on tetrafluoroethylene are stable in the cooking solution, in contrast to sulfonated copolymers of styrene and divinylbenzene, and allow obtaining MCC from millet with a yield of 53 % versus 40 % for the classical method and a degree of polymerization of 440 versus 578, respectively. Due to the destruction of amorphous binders in the MCC's from switchgrass (Panicum virgatum L.), regardless of the conditions of its production, we observe further ordering of the structure of the obtained MCC which is expressed in narrower and more intense peaks in the range 2θ = 22–23°. The FTIR-ATR method showed that the obtained MCC has functional groups similar to commercial M-1021. The AFM method showed that MCC has a globular and wavy relief. Surface roughness with globular relief is 12.6 nm.

Keywords: *microcrystalline cellulose, switchgrass, ion-exchange resin, relief of the surface, Nafion NR-50*

INTRODUCTION

Cellulose is the most common and widely used biopolymer. It is an inexhaustible source of natural fibers, as well as a raw material for the production of microcrystalline (MCC) and powder cellulose, which are widely used in pharmaceutical, food, beverage, cosmetic, chemical and other industries [1–5]. Owing to chemical inactivity, absence of toxicity, high sorption, high strength, flexibility, aspect ratio, the higher thermal stability of MCC in comparison with natural fiber, the stability of cellulose microcrystals aqueous suspensions and great hygroscopicity, the demand for MCC is growing every year [4–10]. Thus, the growth of the world market of MCC from 2018 to 2023 is about 7 % [11], which prompts the improvement of existing methods of obtaining it, as well as the expansion of the raw material base. The most widespread and long-standing is acid hydrolysis of cellulosic materials using aqueous solutions of mainly mineral acids as hydrolyzing agents. This method was first proposed in 1955 by O.A. Batista and P.A. Smith [12]. However, in recent decades, work on obtaining MCC by an organo-solvent method has gained wide publicity, which allows the process to be carried out in one step, as well as to partially or completely exclude mineral acids from the technological process [13–15]. There are also works that suggest replacing mineral acids with solid ones [14–17]. However, there are currently no works on the use of ion exchange resins as solid catalysts for these processes. Therefore, the purpose of our work was to study the structural and morphological characteristics of MCC from switchgrass *(Panicum virgatum L.)* by the method of organo-solvent cooking with the addition of different brands of ion exchange resins instead of sulfuric acid.

MATERIALS AND METHODS

Air-dry switchgrass (*Panicum virgatum L.*), a technical crop (fraction 2–5 mm) from Kyiv region of Ukraine with the characteristics previously described in works [18, 19]. Elemental composition of switchgrass (*Panicum virgatum L.*) is given in Table 1.

MCC was obtained from switchgrass (*Panicum virgatum L.*) by the method of organo-solvent cooking described in [16]. Switchgrass (*Panicum virgatum L.*) was hydrolysed using the solution CH_3COOH (24 wt. %) -H_2O_2 (4 wt. %) and water, along with ion exchange resin. The process was carried out in a round-bottom glass reactor, equipped with a stirrer, reflux condenser, and thermometer, at 105 °C for three hours, with constant agitation and a liquor ratio of 10. Under these conditions of MCC production in a batch reactor, ion-exchange resins were placed in protective bags made of mylar to avoid their mechanical damage. The reaction mixture after reaction was filtered at room temperature and washed repeatedly with distilled water to neutral pH. It was oven-dried at 105 °C for 8 hours. The cellulose yield (*Y*) was calculated using Equation (1) in [20].

As the ion exchange resin was chosen a sulfonated copolymer based on styrene and divinylbenzene Purolite CT-275 (Purolite International Limited, Great Britain, batch no SR 503307/2) and sulfonated copolymer based on tetrafluoroethylene Nafion NR-50 produced by the company E.I. du Pont de Nemours & Co., Inc. (USA) (product code N 03230EI-101), the characteristics of which are given in Table 2 [21]. The use of ion exchange resins in the organo-solvent method of obtaining MCC in a batch reactor requires the use of protective covers for the catalyst to avoid its mechanical damage.

Table 1. Elemental composition of switchgrass (*Panicum virgatum L.*), % (wt.)

H	C	S	N	O
7.48	43.45	0.26–0.33	2.5–2.61	46.13–46.31

Table 2. Characteristics of sulfocationites [21]

Indicator	Value	
	Purolite CT-275	Nafion NR-50
Ionic form (commercial)	H^+	H^+
Density of functional groups per unit mass of dry matter (mg·eq/g)	5.4	0.80
The number of sulfo groups per benzene ring	> 1	–
Mass quota of moisture, % wt., not more	53–57	20–22
Grain size, mm	0.3–1.2	0.18–0.24
The volume quota of the working fraction, % not less	99.0	99.0
Bulk mass, g/dm^3	680.0	1300
Pore size, Å	600–700	–
Maximum operating temperature, °C	145	180

The contents of cellulose, hemicellulose, lignin and other chemical components in cellulosic products were determined by standard chemical analysis, described earlier [22]. All chemical analysis was carried out twice allowing calculating the mean values and standard deviations, which do not exceed 5 %. The inorganic components were determined using Expert 3L XRF (INAM, Ukraine). The degree of polymerization (DP) of cellulose samples was determined by viscosity measurements in a cadmium ethylenediamine solution using an

Ostwald viscometer [23]. The phase identification of the products was examined under X-ray diffraction (XRD) using a MiniFlex 300/600 diffractometer (Rigaku, Japan). The diffraction patterns were recorded using CuK_α radiation (λ = 0.15418 nm), the operating voltage of 40 kV and a current of 15 mA. XRD pattern of samples was obtained in the 2θ range between 2° and 100° with a step of 0.02°. The crystallinity index (CI) [24] was calculated according to Eq. 2 in [21]. FTIR analysis of the obtained cellulose was performed using an IRAffinity-1S FTIR spectrometer (Shimadzu, Japan) equipped with a Quest ATR Diamond GS-10800X (Specac, UK) within the wavenumber range of 4000 to 400 cm^{-1}. The surface morphology was investigated with an atomic force microscope (AFM) NT-206 (Company with double liability “Microtestmachines”, Belarus) equipped with standard sonde CSC37 and rigidity of console 0.3–0.6 N/m. The scan was run in a contact static mode at 10 mcm/s with a step of 0.3 nm. Samples of cellulose (4 mg) were stirred in ethyl alcohol (5 ml) for 15 min. The resulting suspension (0.25 ml) was applied to quartz glass and dried at 50 °C to constant weight. Then the scan was performed on AFM. Thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) were performed with a PT1600 TG-DTA/DSC (STA Simultaneous Thermal Analysis, LINSEIS Messgeräte GmbH, Germany). The samples (13.0±0.1 mg) were collected in a standard corundum pan. The scan was run at 5 °C/min under a flow of air. The mass change was measured from 15.8 to 1000 °C. The sample was analysed three times.

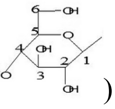
RESULTS AND DISCUSSION

A white, tasteless and odorless MCC was obtained under the earlier described method from switchgrass (*Panicum virgatum L.*). The MCC’s percentage yield was calculated by Eq. 1 [20] (Table 3). The results of the chemical composition of obtained MCC were determined using the above-described methods and the data were summarised in Table 3. It has been found that the yield of MCC on Nafion NR-50 ion exchange resin is 5 % (wt.) higher than on Purolite CT-275 cationite (Table 3). In addition, it has been found that the heterogeneous catalyst Purolite CT-275 in the cooking solution undergoes changes, which become visible in a changing of the resin’s color to light yellow. Therefore, only sulfonated copolymers based on tetrafluoroethylene are stable in the cooking solution, unlike sulfonated copolymers of styrene and divinylbenzene.

Table 3. The main characteristics of obtaining MCC from switchgrass in the presence of ion exchange resins compared to the classical method [19]

Catalyst	Yield of MCC, %	Lignin, % (wt.)	Ash, % (wt.)	Degree of polymerization	CI
Purolite CT-275	47.9	4.3	12.1	483	0.73
Nafion NR-50	53.2	1.4	9.4	441	0.72
H_2SO_4 [19]	40.2	1.2	1.5	577.5	0.74

The X-ray diffraction (XRD) patterns of the MCC from switchgrass on ion exchange resins are presented in Fig. 1. On the diffraction patterns of cellulose samples (Fig. 1) the peaks were observed at: 14–16°; 22–23°; 34–35°, relating to the reflection of the planes 10-1, 101; 002; 040 cellulose crystal lattice, respectively. Peaks in the region $2\theta = 15–16°$ are associated with the diffraction of X-rays from the planes 10-1 and 101 of the crystal lattice of cellulose I. The intensity of the peak reflex in the region $2\theta = 22–23°$ corresponds to the plane 002 of the crystal lattice of natural cellulose I [25]. Profile of amorphous cellulose scattering has a characteristic diffusion character with a maximum of $2\theta = 18.5–19°$ [26]. However, as can be seen from the above diffractograms, the cellulose obtained in the cooking solution with Purolite CT-275 ion exchange resin has additional peaks that are not typical for MCC. This may be due to the partial dissolution of this solid catalyst and its introduction into the final product.

Fig. 2 demonstrates the FTIR-ATR spectra of the obtained MCCs compared to the commercial sample M-1021. In the IR spectra of the MCCs (Fig. 2) there are characteristic absorption bands in the regions of 3000–3600, 2700–3000, 1300–1500, 1000–1200 cm^{-1}, which correspond to the valence vibrations of –OH and –CH, –CH$_2$ groups and deformation and valence vibrations of CO and C-O-C of the cellulose ring, respectively [27–29]. Adsorbed water is manifested by an absorption band in the region of 1630–1640 cm^{-1} [27]. The absence of an absorption band at 1511 cm^{-1}, which is characteristic of the skeletal vibrations of the aromatic ring, indicates a decrease in the amount of lignin in the products. The band in the absorption region at 900 cm^{-1} characterizes asymmetric vibrations in the antiphase and vibrations of the C$_1$ atom and its four surrounding atoms of β-glycoside structures (). This band is called the amorphous band [28]. Its absence indicates the crystalline structure of the obtained samples. Distinct bands in the fields 2918 and 1429–1428 cm^{-1} testify that the sample is characterized by the high degree of the orderliness of macromolecules [29]. In the IR spectra (Fig. 2) of the obtained samples, there are no characteristic absorption bands of phenylpropane units of lignin (1605–1593, 1515–1495, 1470–1460 cm^{-1}). This indicates the occurrence of deep oxidative transformations of phenolic structures and effective diffusion of delignification products into the solution under the conditions of the experiment [27–30].

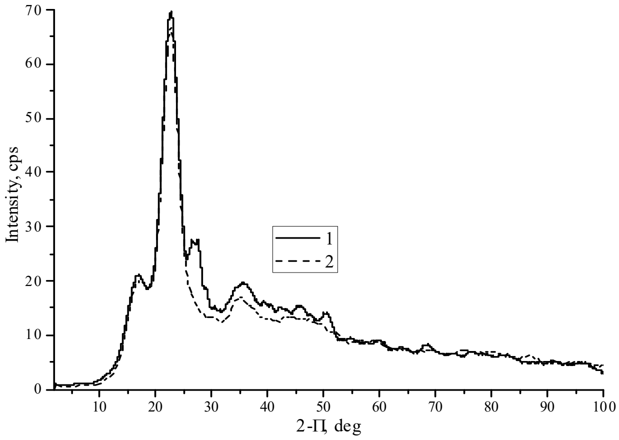


Fig. 1. XRD patterns of MCC obtaining from switchgrass (*Panicum virgatum L.*) in the presence of ion exchange resins: *1* – Purolite CT-275, *2* – Nafion NR-50

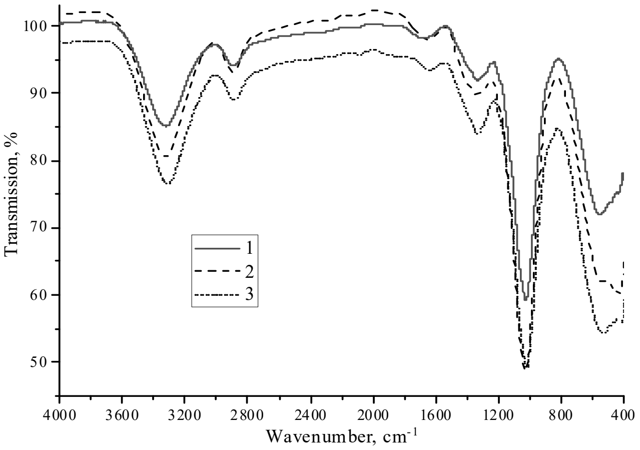
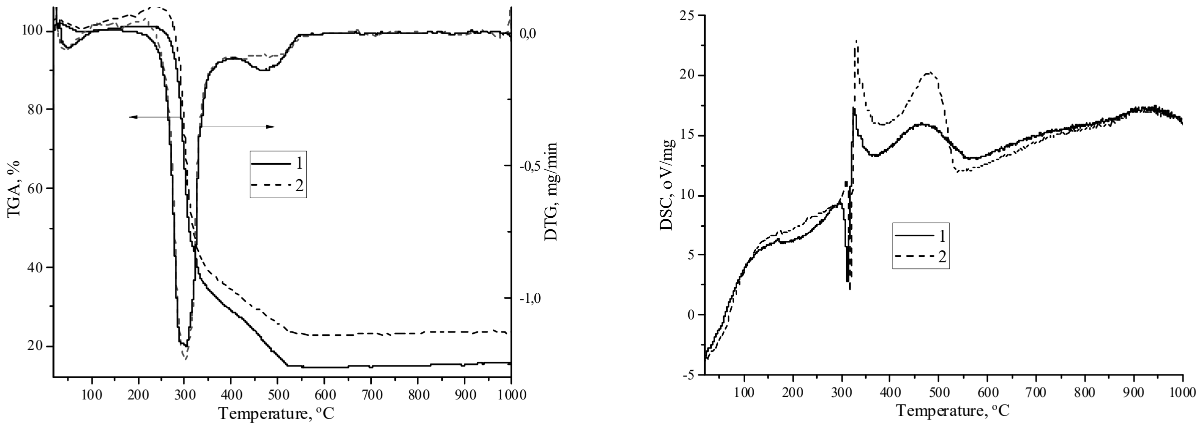


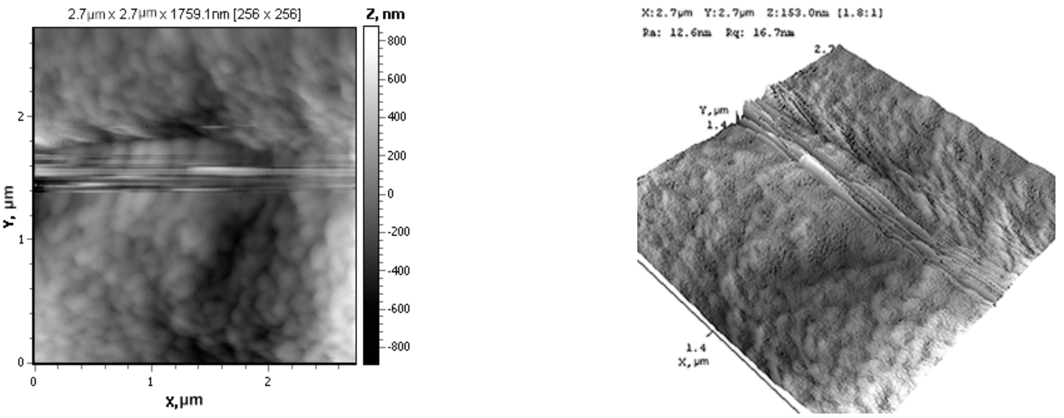
Fig. 2. FT-IR spectra of MCC obtaining from switchgrass in the presence of ion exchange resins: *1* – Purolite CT-275, *2* – Nafion NR-50 compared to commercial M-1021 (*3*)

Thermogravimetric analysis (TGA), derivative thermogram (DTG) and differential scanning calorimetry (DSC) from temperature for MCC obtained from switchgrass on different ion exchange resins are presented in Fig. 3. The DSC signal was measured together with the TGA curve. The initial slight weight loss (about 1–4 % up to 120 °C) occurs due to evaporation and dehydration of adsorbed and surface water. In addition, a sharp weight loss started at 225 and ended at 370 °C, which was attributed to the endothermic formation of anhydrocellulose [31]. This is agreement with the DSC (Fig. 3 *b*) curves. A slow weight loss up to 530 °C, which was attributed to the complete thermal decomposition of cellulose, resulting in the decomposition of glycosyl units followed by their conversion to carbon [31]. It was observed that the residue remaining after decomposition was 14.7 and 22.7 % for MCC prepared on Purolite CT-275 and Nafion NR-50 ion exchange resins, respectively. This two-step process is also well reflected in the two DSC peaks presented in Fig. 3 *b*, and two DTG derivative peaks (Fig. 3 *a*). DTG (Fig. 3 *a*) and DSC (Fig. 3 *b*) curves show that cellulose samples should not be heated above 220 °C. The peak of the decomposition temperature of the samples is visible on the derivative curve of weight loss (Fig. 3 *a*). The main peak decomposition temperature of MCC is 299 and 300 °C for MCC obtained on Purolite CT-275 and Nafion NR-50 ion exchange resins, respectively, which is in good agreement with the literature data [32–35].



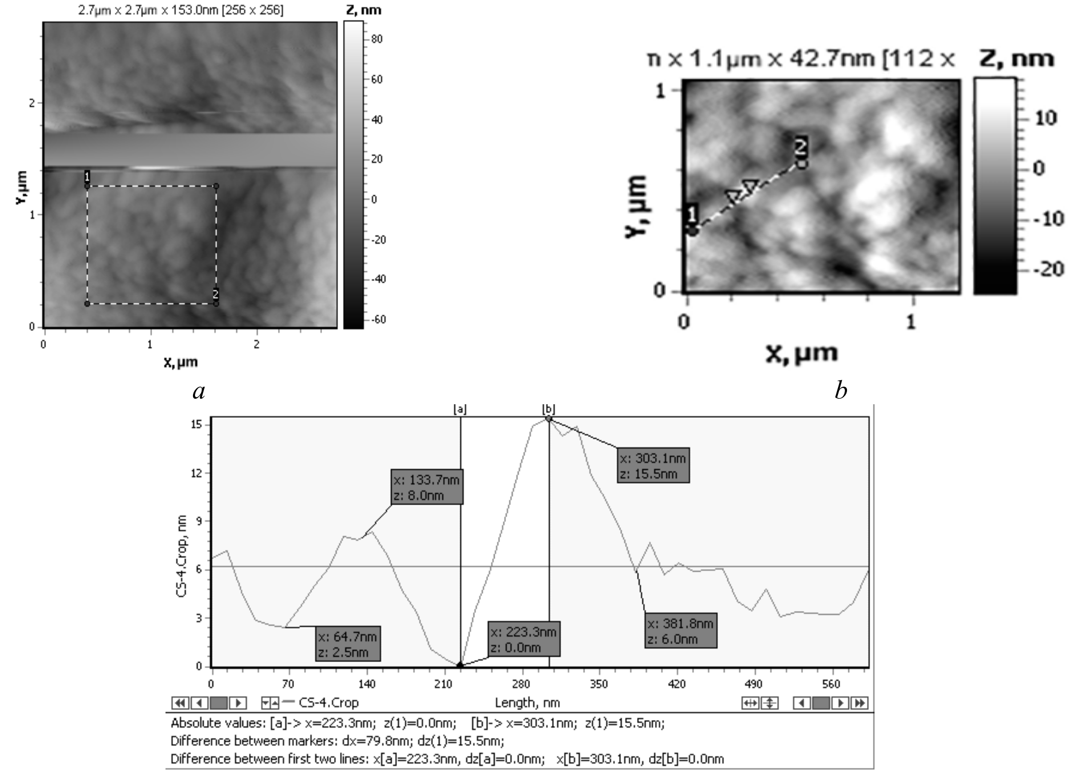
a *b*

Fig. 3. TGA and DTG (*a*) and DSC (*b*) curves MCC obtaining from switchgrass in the presence of ion exchange resins: *1* – Purolite CT-275, *2* – Nafion NR-50



a *b*

Fig. 4. 2D (*a*) and 3D (*b*) image of the MCC film's surfaces isolated from switchgrass on ion exchange resin Nafion NR-50

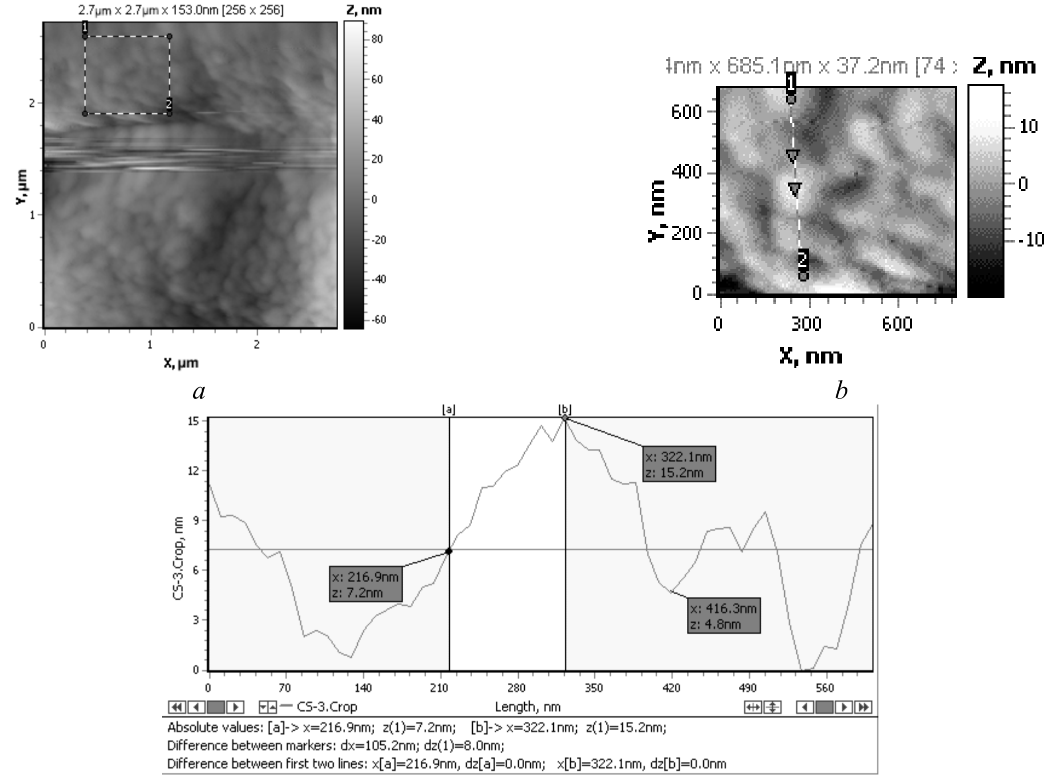


Absolute values: [a]-> x=223.3nm; z(1)=0.0nm; [b]-> x=303.1nm; z(1)=15.5nm;
Difference between markers: dx=79.8nm; dz(1)=15.5nm;
Difference between first two lines: x[a]=223.3nm, dz[a]=0.0nm; x[b]=303.1nm, dz[b]=0.0nm

a *b*

c

Fig. 5. 2D (*a*) images of the MCC film's surfaces isolated from switchgrass on ion exchange resin Nafion NR-50 with the selected fragment of the globule, as well as fragment (*b*) with the line of intersection of the particles and its profile (*c*)

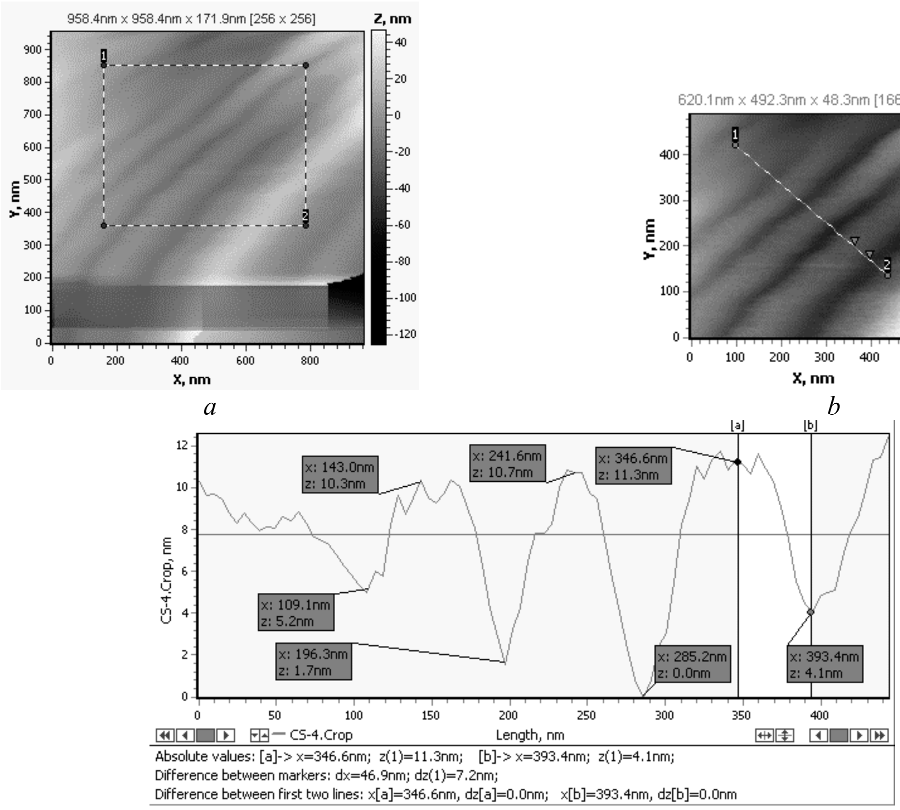


Absolute values: [a]-> x=216.9nm; z(1)=7.2nm; [b]-> x=322.1nm; z(1)=15.2nm;
Difference between markers: dx=105.2nm; dz(1)=8.0nm;
Difference between first two lines: x[a]=216.9nm, dz[a]=0.0nm; x[b]=322.1nm, dz[b]=0.0nm

a *b*

c

Fig. 6. 2D (*a*) images of the MCC film's surfaces isolated from switchgrass on ion exchange resin Nafion NR-50 with the selected fragment of the globule, as well as fragment (*b*) with the line of intersection of the particles and its profile (*c*)



a *b*

c

Fig. 7. 2D (*a*) images of the MCC film's surfaces isolated from switchgrass on ion exchange resin Nafion NR-50 with a selected fragment of the wavy relief, as well as fragment (*b*) with the line of intersection of the particles and its profile (*c*)

Fig. 5 shows a 2D (*a*) image of the surface with a selected fragment, as well as the fragment itself (*b*) with a cross-section line along the globules and its profile (*c*). The last image shows that the globules have a diameter of 5.5; 15.5 nm and lengths of 158.6 and 158.5 nm, respectively.

Fig. 4 *a* shows the surface topography of the MCC film synthesized from switchgrass on Nafion NR-50 ion exchange resin. The globular relief of the film surface is clearly visible (Fig. 4 *a*, *b*). The surface roughness is 12.6 nm.

Fig. 6 presents a 2D image of the surface (*a*) with another selected fragment on this scan, as well as the fragment itself (*b*) with a globular section line and its profile (*c*). From the last image, it can be seen that the globules have a diameter of 8.0 nm and a length of 196.4 nm, respectively.

In Fig. 7 shows a 2D (*a*) image of another part of the relief on a scan measuring 958.4×958.4 nm. As can be seen from the scan, it has a wavy topography. Highlighted area: tracks resembling oriented fibers. When conducting a section of these tracks (Fig. 7 *b*) and analyzing the corresponding profile (Fig. 7 *c*), it can be found that their width is: 87.3; 88.9; 108.1 nm, and height: 8.6, 10.7, 7.2 nm.

CONCLUSION

The possibility of replacing sulfuric acid in the organo-solvent method of obtaining microcrystalline cellulose with ion-exchange resins was investigated for the first time. The sulfonated copolymer of styrene and divinyl benzene with two functional groups per ring – Purolite CT-275 and the sulfonated copolymer based on tetrafluoroethylene - Nafion NR-50 were chosen as the initial ion exchange resins. It is shown that the use of ion-exchange resins in the organic-solvent method of obtaining MCC in a batch reactor requires the use of protective covers for the catalyst to avoid its mechanical damage. It has been found that only sulfonated copolymers based on tetrafluoroethylene are stable in the cooking solution, in contrast to sulfonated copolymers of styrene and divinylbenzene, and allow obtaining MCC from millet with a yield of 53 % versus 40 % for the classical method (with sulfuric acid) and a degree of polymerization of 440 versus 578, respectively. The last one was also confirmed by the absence of an absorption band at 1605–1593, 1515–1495, 1511, and 1470–1460 cm^{-1} in FTIR-ATR spectra. The method of thermogravimetric analysis shows that the MCC obtained using solid catalysts does not differ in terms of thermal parameters from the known literature data characteristic of the MCC obtained by other methods. Thus, the carried out studies showed that the ion-exchange resins use allows obtaining MCC with similar characteristics as MCC on liquid catalysts.

ACKNOWLEDGEMENTS

We thank the Armed Forces of Ukraine for safety to carry out this work. This work was only possible thanks to the resilience and courage of the Ukrainian Army.

Фізико-хімічні характеристики мікрокристалічної целюлози з проса прутовидного (*Panicum virgatum L.*), одержаної в присутності твердого каталізатора

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Основною ідеєю даної роботи є дослідження структурних та морфологічних характеристик мікрокристалічної целюлози з проса прутовидного (Panicum virgatum L.) методом органо-сольвентної варки з додаванням різних марок іонообмінних смол замість сірчаної кислоти. Як вихідні іонообмінні смоли обрано сульфований співполімер стиролу та дивінілбензолу з двома функціональними групами на одне кільце – Purolite CT-275 та сульфований сополімер на основі тетрафторетилену – Nafion NR-50. Для дослідження обрано технічну культуру - висушене на повітрі прутовидне просо (Panicum virgatum L.). З нього одержали мікрокристалічну целюлозу (МКЦ) методом органосольвентного варіння з додаванням твердого каталізатора. За допомогою методів XRD, XRF, FTIR-ATR, AFM, TGA та DSC досліджено структуру та морфологію МКЦ. Було виявлено, що використання іонообмінних смол при органо-сольвентному способі одержання МКЦ у реакторі періодичної дії вимагає застосування захисних чохлів для каталізатора, щоб уникнути його механічного пошкодження. Встановлено, що лише сульфовані сополімери на основі тетрафторетилену є стійкими у варочному розчині, на відміну від сульфованих сополімерів стиролу та дивінілбензолу, і дозволяють одержати МКЦ з проса з виходом 53 % проти 40 % для класичного способу і ступенем полімеризації 441 проти 578, відповідно. Завдяки руйнуванню аморфних в'яжучих у МКЦ з проса прутовидного (Panicum virgatum L.), незалежно від умов його виробництва (на твердому чи рідкому каталізаторі), спостерігається подальше впорядкування структури отриманої МКК, що виражається в більш вузьких і інтенсивніших піках в діапазоні 2θ = 22-23°. Методом FTIR-ATR показано, що отримана МКЦ має функціональні групи, аналогічні комерційній М-1021. Методом AFM показано, що МКК має глобулярний та хвилеподібний рел'єф. Шорсткість поверхні при глобулярному рельєфі складає 12.6 нм.

***Ключові слова**: мікрокристалічна целюлоза, просо прутовидне, іонообмінна смола, рельєф поверхні, Nafion NR-50*

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Received 07.09.2023, accepted 19.02.2024