DOI: 10.6060/ivkkt.20196212.5984

УДК: 54.05+544.77

ПОЛУЧЕНИЕ НАНОКРИСТАЛЛИЧЕСКОЙ ЦЕЛЛЮЛОЗЫ ГИДРОЛИЗОМ В СМЕСИ СОЛЯНОЙ И АЗОТНОЙ КИСЛОТ

Н.В. Рублева, Е.О. Лебедева, А.В. Афинеевский, М.И. Воронова, О.В. Суров, А.Г. Захаров

Наталья Викторовна Рублева, Марина Игоревна Воронова, Олег Валентинович Суров*, Анатолий Георгиевич Захаров

Лаборатория физической химии гетерогенных систем полимер-жидкость, Институт химии растворов им. Г.А. Крестова РАН, ул. Академическая, 1, Иваново, Российская Федерация, 153045
E-mail: rublevanw@yandex.ru, miv@isc-ras.ru, ovs@isc-ras.ru*, agz@isc-ras.ru

Екатерина Олеговна Лебедева

Факультет фундаментальной и прикладной химии, Ивановское отделение Высшего химического колледжа РАН, Ивановский государственный химико-технологический университет, просп. Шереметевский, 7, Иваново, Российская Федерация, 153000

Андрей Владимирович Афинеевский

Кафедра физической и коллоидной химии, Ивановский государственный химико-технологический университет, просп. Шереметевский, 7, Иваново, Российская Федерация, 153000
E-mail: afineevskiy@mail.ru

В работе применен гидротермальный метод получения нанокристаллической целлюлозы (НКЦ) в смеси соляной и азотной кислот при молярном соотношении 8:2, 7:3, 6:4 и 5:5. Гидролиз сульфатной целлюлозы в смеси азотной и соляной кислот проводили в герметичном толстостенном сосуде из нержавеющей стали с тефлоновым вкладышем в течение 3 ч при 110 °С. Свойства НКЦ охарактеризованы с использованием различных методов: элементного анализа, термогравиметрического анализа, ИК спектроскопии, поляризационной оптической и электронной сканирующей микроскопии, метода динамического рассеяния света. Определен выход НКЦ, размер и заряд частиц, степень полимеризации, температура термодеструкции, изучена морфология образцов. Самый высокий выход (32 %) наблюдается при соотношении соляной и азотной кислот 7:3. Найдено, что частицы НКЦ имеют сферическую форму со средним размером 60-80 нм. Сделано предположение, что в присутствии сильного окислителя происходит гидролиз не только аморфных областей целлюлозы, но и частично кристаллических, что сказывается на конечной форме частиц НКЦ. Показано, что гидролиз в смеси соляной и азотной кислот вызывает окисление первичных гидроксильных групп пиранозного кольца целлюлозы и образование поверхностных карбоксильных групп. Водные суспензии НКЦ демонстрируют высокую коллоидную стабильность вследствие достаточно большого поверхностного заряда. Отмечается значительное повышение термической устойчивости НКЦ по сравнению с образцом НКЦ, полученным стандартным сернокислотным гидролизом: температура термического разложения увеличивается на 130-148 °С.

Ключевые слова: нанокристаллы целлюлозы, гидротермальный метод, физико-химические свойства, термическая устойчивость

Для цитирования:

Рублева Н.В., Лебедева Е.О., Афинеевский А.В., Воронова М.И., Суров О.В., Захаров А.Г. Получение нанокристаллической целлюлозы гидролизом в смеси соляной и азотной кислот. *Изв. вузов. Химия и хим. технология*. 2019. Т. 62. Вып. 12. С. 85–93

For citation:

Rubleva N.V., Lebedeva E.O., Afineevskii A.V., Voronova M.I., Surov O.V., Zakharov A.G. Production of cellulose nanocrystals by hydrolysis in mixture of hydrochloric and nitric acids. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*. 2019. V. 62. N 12. P. 85–93

PRODUCTION OF CELLULOSE NANOCRYSTALS BY HYDROLYSIS IN MIXTURE OF HYDROCHLORIC AND NITRIC ACIDS

N.V. Rubleva, E.O. Lebedeva, A.V. Afineevskii, M.I. Voronova, O.V. Surov, A.G. Zakharov

Natalia V. Rubleva, Marina I. Voronova, Oleg V. Surov*, Anatoly G. Zakharov

Laboratory of Physical Chemistry of Polymer-Liquid Heterogeneous Systems, G.A. Krestov Institute of Solution Chemistry of the RAS, Akademicheskaya st., 1, Ivanovo 153045, Russia
E-mail: rublevanw@yandex.ru, miv@isc-ras.ru, ovs@isc-ras.ru*, agz@isc-ras.ru

Ekaterina O. Lebedeva

High Chemistry College, Ivanovo State University of Chemistry and Technology, Sheremetievskiy ave., 7, Ivanovo, 153000, Russia

Andrei V. Afineevskii

Department of Physical and Colloid Chemistry, Ivanovo State University of Chemistry and Technology, Sheremetievskiy ave., 7, Ivanovo, 153000, Russia
E-mail: afineevskiy@mail.ru

In this work, cellulose nanocrystals (CNC) have been produced by hydrothermal method in a mixture of hydrochloric and nitric acids in molar ratios of 8:2, 7:3, 6:4 and 5:5. Hydrolysis of sulphate cellulose in the mixtures of nitric and hydrochloric acids was conducted in a sealed thick-walled stainless steel vessel with a teflon insert for 3 h at 110 °C. Properties of CNC have been characterized by applying different methods: elemental analysis, thermogravimetric analysis, IR spectroscopy, polarization optical microscopy, scanning electron microscopy, and dynamic light scattering. Yield of CNC, size and charge of the CNC particles, degree of polymerization, temperature of thermal destruction have been determined, and morphology of the CNC samples has been characterized. The highest CNC yield (32%) has been observed at a 7:3 ratio of nitric and hydrochloric acids. It has been established that the CNC particles are spherical and have an average size of 60-80 nm. An assumption has been made that presence of a strong oxidant (nitric acid) may cause hydrolysis of both amorphous and crystalline (in part) regions of cellulose, which affects the final shape of the CNC particles. It has been shown that the hydrolysis in a mixture of nitric and hydrochloric acids causes an oxidation of primary hydroxyl groups of the cellulose pyranose ring and formation of surface carboxyl groups. The CNC aqueous suspensions demonstrate high colloidal stability due to a rather high surface charge. It is noted that the CNC thermal stability is much higher than that of the CNC samples obtained by the standard sulfuric acid hydrolysis: the temperature of thermal destruction increases by 130-148 °C.

Key words: cellulose nanocrystals, hydrothermal method, physicochemical properties, thermal stability

INTRODUCTION

Cellulose is a natural polymer, the most important representative of polysaccharides with macromolecules consisting of D-glucose units linked by a glycosidic bond. An elementary unit of cellulose has a structure of a six-member oxygen-containing heterocycle, and the formation of the glycosidic bond between the elementary units involves, along with an aldehyde group located at the first carbon atom of one elementary unit, a hydroxyl group at the fourth carbon atom of the neighboring unit [1, 2]. The glycosidic bond in the cellulose macromolecule has a β-configuration (denoting a bond with an opposite spatial orientation in comparison with the configuration of the asymmetric carbon atom C-5 in the glucose molecule).

Glycosidic bonds are comparatively easily split by acid hydrolysis, which is responsible for the relative susceptibility of cellulose to the action of aqueous solutions of acids. Complete hydrolysis of cellulose produces *D*-glucose.

In terms of formation of different derivatives, cellulose can be considered a polymeric polyatomic alcohol with the macromolecule of the elementary units containing three hydroxyl groups: a primary one – at the sixth carbon atom – and two secondary ones – at the second and third carbon atoms. The elementary unit of the cellulose macromolecule is in the energetically more favourable “armchair” $^4C_1$ conformation, in which the hydroxyl and hydroxymethyl groups are equatorial, i.e. they are located approximately in the plane formed by the second, third and fifth carbon atoms and the oxygen atom of the pyranose cycle. Such position makes them highly reactive [3, 4].

Along with the ability to participate in chemical reactions, the role of hydroxyl groups also consists in forming a system of intra- and intermolecular hydrogen bonds. The primary elements of the supramolecular structure of cellulose are long and thin nano-size threads – elementary fibrils. Nanofibrils of natural cellulose are formed by biosynthesis in living cells of plants, algae and some bacteria and animals (crustacea, cochleae and tunicates). Elementary nanofibrils have lateral dimensions of 3-10 nm depending on the cellulose origin. According to the model of amorphous-crystal structure of nanofibrils, cellulose macromolecules lie along the fibrils forming alternating regions with different ordering degrees – crystalline and amorphous ones. The share and sizes of crystalline regions depend on cellulose origin.

Acid treatment leads to selective hydrolysis of cellulose amorphous regions. Treatment with dilute acids produces microcrystalline cellulose (the size of particles is tens and hundreds of microns), while treatment with concentrated acids allows obtaining cellulose nanocrystals (CNC) [5, 6]. CNC particles have an anisotropic shape. The sizes of the obtained CNC particles, depending on the cellulose origin and hydrolysis conditions, vary from 50 to 1100 nm in length and approximately from 3 to 50 nm in diameter.

CNC attract a lot of attention of researchers due to their physical and chemical properties, such as nontoxicity and biocompatibility, biodegradation, large specific surface area, high elasticity modulus, and optical characteristics. The use of CNC as a filler in polymers makes it possible to impart new qualities to materials: to improve their mechanical, optical, absorption properties, and biodegradation [7-10].

The standard procedure of obtaining CNC includes hydrolysis with 62-65 % sulfuric acid at 45-50 °C, removing the acid by applying repeated cycles of centrifugation, dialysis, ultrasound treatment. After washing, a pH value of the suspension is around 2.4 due to surface groups $–OSO_3H$ [11]. By conducting controlled hydrolysis with sulfuric acid (due to partial etherification of the cellulose hydroxyl groups), it is possible to graft sulfate groups onto the surface of cellulose crystallites and obtain stable suspensions, mainly, due to the electrostatic repulsion between the negatively charged particles. The main disadvantage of this method is that the substitution of cellulose surface hydroxyls with sulphate groups as a result of sulfuric acid hydrolysis does not only increase the stability of the CNC aqueous suspensions but also reduces thermal stability of the CNC and the CNC based composites (due to pyrolysis catalyzed by surface sulfogroups) [12, 13]. Besides, sulfuric acid hydrolysis does not only remove the amorphous part of cellulose but also changes the ratio of the geometric parameters of nanocrystals and increases their polydispersity, which has a negative effect on the composites strength. Moreover, the CNC production is costly and environmentally unsafe.

In order to find an alternative, cellulose hydrolysis in the presence of different mineral (hydrochloric, phosphoric, hydrobromic, heteropolyacids) [14-17], carboxylic (formic, acetic, oxalic, citric, maleic) and organic acids (*p*-toluenesulfonic, benzenesulfonic) and their mixtures has been studied [18, 19].

However, the attempts to replace sulfuric acid usually lead to limited dispersibility of CNC in polar media and increase the flocculation of aqueous suspensions due to an insufficient surface charge of the CNC particles. Therefore, in this case hydrolysis is often combined with preliminary or subsequent oxidation of cellulose [20]. Cellulose oxidation is accompanied by the formation of surface carboxyl groups and reduction in the degree of polymerization of cellulose [21]. Besides, the presence of oxidized (aldehyde or carboxyl) groups in the cellulose macromolecule can increase the hydrolysis rate [2].

Cellulose oxidation is often conducted with 2,2,6,6-tetramethylpiperidine-1-yl)oxyl) (TEMPO) and other oxidants (such as hydrogen peroxide, ammonium persulfate, $NaNO_2$-HNO_3 and others) [22-26]. The formation of surface carboxyl groups during oxidation improves the dispersibility of CNC suspensions in polar media, including polymer matrices of composites. A very important circumstance is that, unlike sulfate groups, surface carboxyl groups do not reduce the thermal stability of CNC and CNC-based composites.

A recently published paper describes a one-step method of producing carboxylated CNC from microcrystalline cellulose (MCC) using a mixture of inorganic acids [27]. This approach allows, under hydrothermal conditions of hydrolysis in a mixture of nitric and hydrochloric acids, to obtain stable suspensions of CNC with a high content of surface carboxyl groups.

The aim of this work is to produce CNC under hydrothermal conditions of sulphate cellulose hydrolysis in a mixture of hydrochloric and nitric acids and to study the physicochemical properties of the synthesized CNC.

EXPERIMENTAL PART

Materials

The original materials for obtaining CNC were sulphate bleached pulp of coniferous wood GOST (State Standard) 9571-89, sulfuric acid (chemically pure, GOST (State Standard) 4204-77, Chimmed), hydrochloric acid (especially pure, GOST (State Standard) 14261-77, Sigma-Tech) and nitric acid (chemically pure, GOST (State Standard) 4461-77, Chimmed).

Production of CNC by sulfuric acid hydrolysis

Aqueous suspensions of CNC were obtained by sulfuric acid hydrolysis of sulphate cellulose by the method described earlier [13]. The hydrolysis (sulphate cellulose concentration of 0.025 g/ml) was conducted in a solution of sulfuric acid (62%) at 50 °C for 2 h at intensive mixing. After the hydrolysis, the suspension was washed with water with subsequent centrifugation (for 10 mins at 8000 rpm). The centrifugation was stopped after 5-6 washings. Then the CNC suspension was purified with ion-exchange resin (TOKEM MB-50(R) and treated with ultrasound (Sonorex DT100, Bandelin, Germany) for 15-30 min. The CNC yield was about 30%.

Obtaining of CNC by hydrothermal method in a mixture of nitric and hydrochloric acids

Hydrolysis of sulphate cellulose in a mixture of nitric and hydrochloric acids was performed in a sealed thick-walled stainless steel vessel with a teflon insert. The hydrolysis of 1 g of sulphate cellulose in 27 ml of the mixture was conducted for 3 h at 110 °C with different molar ratios of the acids (HCl/HNO_3) (8: 2; 7: 3; 6: 4 and 5: 5) maintaining the total concentration of the aqueous solution at 4 M.

After cooling to room temperature, the obtained CNC suspension was diluted with distilled water and then repeatedly (5-6 times) washed by successive centrifugation. After that, the CNC suspension was treated with ultrasound (Sonorex DT100 Bandelin) for 15-30 min. The purification of the CNC aqueous suspension was conducted by using ion-exchange resin TOKEM MB-50(R) for 72 h. The CNC yield was from 10 to 32%.

Determining of CNC yield

The CNC yield was determined by a gravimetric method. For this, the CNC suspension was filtered on a pre-weighed glass fiber filter MN GF-1 (Macherey-Nagel, Germany) with a retention capacity of over 0.7 μm. Then the filter was dried at 100 °C for 2 h, and the sediment mass of the particles exceeding 0.7 μm was determined by a weight gain. To remove water-soluble low-molecular compounds from CNC suspensions, dialysis treatment of the suspensions was performed. For that, the filtered suspension was placed in a dialysis membrane (pore size of 14 kDa, Roth). Then the membrane with the CNC suspension was placed in a vessel with a bidistilled water. The dialysis was performed for 5-7 days, periodically replacing the water in the vessel until a constant pH value was reached. The CNC suspension was collected and its volume was determined. Several parallel samples of accurately measured volume were taken, poured into pre-weighed Petri dishes and dried in air to constant weight. Knowing a concentration and a volume of the CNC suspension, the total yield of the CNC can be calculated taking into account the mass of the initial cellulose. The relative error of the CNC yield measurement in three parallel experiments did not exceed 2.5%.

Methods of research

The CNC sample films for thermogravimetric analysis (TG), infrared spectroscopy (IR), polarizing optical microscopy (POM) and scanning electron microscopy (SEM) were obtained by natural evaporation of water at room temperature from aqueous suspensions with a concentration of 10 g/l.

TG analysis was carried out on a TG 209 F1 Iris thermomicrobalance (Netzsch, Germany) using platinum crucibles in a dry argon at a transmission rate of 30 ml/min and a heating rate of 10 K/min.

IR spectra were obtained on a VERTEX 80v spectrophotometer (Bruker, Germany) in the frequency range of 4000-400 cm^{-1}. Samples were pressed into tablets containing 1 mg of an analyte and 100 mg of potassium bromide.

The sample films were studied using a Soptop CX40P polarizing optical microscope (Sunny Instruments, China).

To study a morphology of the CNC samples, we used a VEGA3 TESCAN scanning electron microscope (Czech Republic). The samples were analyzed at an accelerating voltage of 5 kV in the high vacuum mode.

The CNC particle sizes in aqueous suspensions were determined by the method of dynamic light scattering (DLS) (radiation wavelength 633 nm) on a Zetasizer Nano ZS (Malvern Instruments Ltd, UK) operating in the range of 0.3 nm-6 μm. The measurements were carried out at 20 °C in disposable polystyrene cells at a suspension concentration of 0.1 mg/ml. The obtained particle size values are the results of averaging over five consecutive measurement cycles. In turn, the value obtained in each cycle is the result of automatic processing of 10-15 measurements.

The sizes of the CNC particles measured by the DLS method are the averaged values for hydrodynamic diameters of equivalent spheres and do not reflect the real physical dimensions of anisotropic CNC rod-like particles, but are used for comparison [28]. However, as shown in [29], the hydrodynamic diameters measured by the DLS method strictly correlate with the lengths of anisotropic CNC particles obtained from transmission electron microscopy (TEM) and atomic force microscopy (AFM) images. Analysis of the literature shows the recent trend of an increasing use of the DLS method due to its simplicity and accessibility [30, 31].

A surface charge of the CNC particles in aqueous suspensions was estimated from a ζ-potential value (Zetasizer Nano ZS). The obtained ζ-potential values are the result of averaging over five successive measurement cycles.

Concentration of surface sulfate groups of the CNC obtained by sulfuric acid hydrolysis was evaluated by elemental analysis for sulfur content (Flash Analyzer EA-1112, Thermo Quest, Italia).

Aqueous solution of ethylenediamine cadmium complex (cadoxen) was used for dissolving cellulose samples and testing their viscosity and degree of polymerization (DP) [32, 33]. The DP was calculated from the intrinsic viscosity values, as follows:

$$DP^{\alpha} = [\eta]/K$$

where K = 0.71; $\alpha = 0.94$ (for DP<1900).

According to the Huggins equation, the intrinsic viscosity (100 ml/g) equals:

$$[\eta] = [(2\eta_{sp}+1)^{1/2} - 1]/c$$

where η_{sp} is specific viscosity of a polymer solution; c is a concentration of the polymer in the solution (g/100 ml).

The specific viscosity η_{sp} can be derived as follows:

$$\eta_{sp} = t/t_0 - 1$$

where t_0 is an efflux time of the solvent (cadoxen) in seconds; t is an efflux time of the cellulose solution (s).

The specific viscosity (η_{sp}) can be measured in an Ostwald or Ubellode capillary viscometer. In this case, the efflux time of the solvent should be at least 100 s. According to the above formula, it is possible to calculate the intrinsic viscosity by a single value of the specific viscosity (method of determining [η] by one point). However, the method is accurate enough only if there is a linear relationship between c and η_{sp}/c.

To prepare a solution of cadoxen, 1000 ml of 28% ethylenediamine were cooled to -3-5 °C. Then, 80 g of CdO were added to the ethylenediamine solution at vigorous stirring and the mixture was kept for 2h at -3-5 °C. Thereafter, the cadoxen solution was separated from residual solid by decantation or centrifugation.

About 0.1 g of a cellulose sample was dissolved in 100 ml of cadoxen. The cellulose solution was drawn into a viscometer, equilibrated in a water bath to 20 °C for 30 min and then the efflux time was measured.

RESULTS AND DISCUSSION

Yield, size, shape and charge of CNC particles depend on acid nature and concentration, as well as temperature and duration of hydrolysis [9]. Hydrothermal conditions provide high temperature and pressure in a system, which reduce hydrolysis duration and increase the CNC yield [14, 27]. Nitric acid as a strong oxidant causes oxidation of primary hydroxyl groups of the cellulose pyranose ring and formation of surface carboxyl groups.

Characteristics of the CNC samples obtained by the standard sulfuric acid hydrolysis and hydrothermal method in a mixture of hydrochloric and nitric acids are presented in Table 1.

Table 1

Characteristics of CNC samples

***Таблица 1*. Характеристики образцов НКЦ**

Characteristics	[a]Sample				
	CNC (H_2SO_4)	CNC (8:2)	CNC (7:3)	CNC (6:4)	CNC (5:5)
Yield, %	30	10	32	23	18
Sulfur content, %	0.75	-	-	-	-
Hydrodynamic diameter of particles in an aqueous suspension, nm:					
first fraction	45	105	85	75	80
second fraction	260	-	-	400	350
ζ-potential, mV	-53	-23	-40	-35	-28
Degree of polymerization	80	50	100	80	100
[b]The peak temperature of degradation (T_{max}), °C	170	300	309	318	306

Notes: [a] notation CNC (H_2SO_4) corresponds to the sample obtained by the standard sulfuric acid hydrolysis. The samples CNC (8:2), CNC (7:3), CNC (6:4) and CNC (5:5) have been obtained by hydrothermal method in a mixture of hydrochloric and nitric acids with a molar ratio $HCl:HNO_3$ of 8:2, 7:3, 6:4 and 5:5, respectively.

[b] The temperature of the maximum mass loss rate was taken as the peak temperature of degradation (T_{max}).

Примечания: [a] обозначение CNC (H_2SO_4) соответствует образцу, полученному стандартным сернокислотным гидролизом. Образцы CNC (8:2), CNC (7:3), CNC (6:4) и CNC (5:5) были получены гидротермальным методом в смеси серной и азотной кислот с молярным отношением $HCl:HNO_3$ 8:2, 7:3, 6:4 и 5:5, соответственно.

[b] температура максимальной скорости потери массы была взята как максимальная температура разложения (T_{max}).

The yield of the CNC obtained in a mixture of hydrochloric and nitric acids under hydrothermal conditions, in general, is lower than that in the standard sulfuric acid hydrolysis. The highest yield (32%) is observed at a 7:3 ratio of hydrochloric and nitric acids. This result is in the strong contradiction with the results obtained by Cheng et al. [27]. In [27] the concentration ratio of 7:3 is characterized by lowest yield in the row of 9:1; 8:2; 7:3; 6:4 and 5:5 ratios. However, the authors of Ref. [27] do not indicate clearly how they calculated the yield of CNC. Some authors really postulate a high yield of CNC as a result of cellulose hydrolysis with hydrochloric acid (for instance, see [34-36]). However, hydrolysis with HCl does not introduce any charges on the cellulose surface, and the isolation of CNC from the hydrolyzed cellulose matrix cannot be performed by mere dispersion in water. In our case, we are talking about the CNC, aqueous suspensions of which have a high colloidal stability due to a sufficiently large surface charge (see section *Determining of CNC yield*).

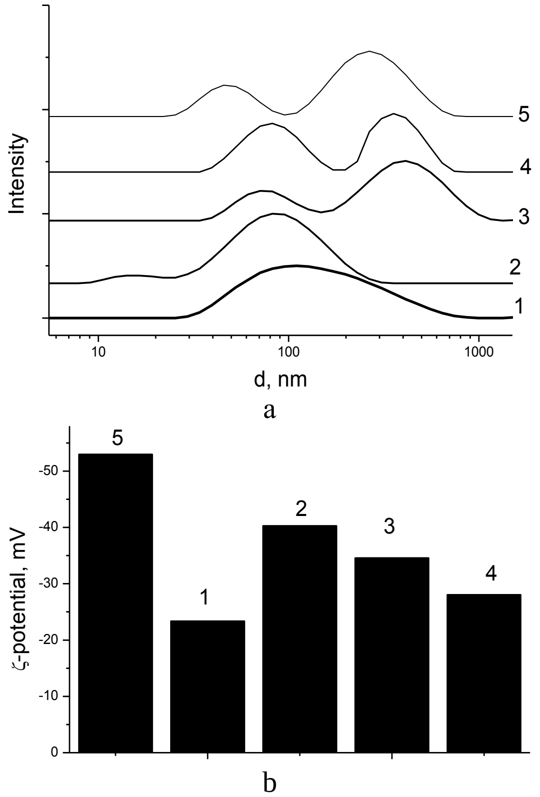


Fig. 1. Hydrodynamic diameters (a) and surface charges (b) of particles in aqueous suspensions of CNC samples: 1 - CNC (8:2); 2 - CNC (7:3); 3 - CNC (6:4); 4 - CNC (5:5); 5 - CNC (H_2SO_4)

Рис. 1. Гидродинамические диаметры (a) и поверхностные заряды (b) частиц в водных суспензиях для образцов НКЦ: 1 - НКЦ (8:2); 2 - НКЦ (7:3); 3 - НКЦ (6:4); 4 - НКЦ (5:5); 5 - НКЦ (H_2SO_4)

Experimental data on DLS in CNC aqueous suspensions indicate polydisperse character of the CNC particle size distribution. One can distinguish two groups of the particles with sizes of about 50-100 and 300-400 nm, respectively (Table 1, Fig. 1). As a HCl content in a mixture of the acids increases (7: 3 and 8: 2), a fraction with the larger particle size disappears, while the remaining fraction has a particle size of about 100 nm. Increasing a hydrochloric acid content in the mixture lowers cellulose degree of polymerization as well (Table 1).

The CNC aqueous suspensions exhibit high colloidal stability for a long time, and no flocculation is observed during storage for more than a month. That is caused by a significant surface charge of the sulfate or carboxyl groups grafted onto the CNC particles surface during sulfuric acid hydrolysis, or hydrolysis in a mixture of HCl and HNO_3, respectively (Table 1, Fig. 1).

The formation of surface carboxyl groups during hydrolysis in a mixture of the acids is confirmed by IR spectra of CNC samples (Fig. 2).

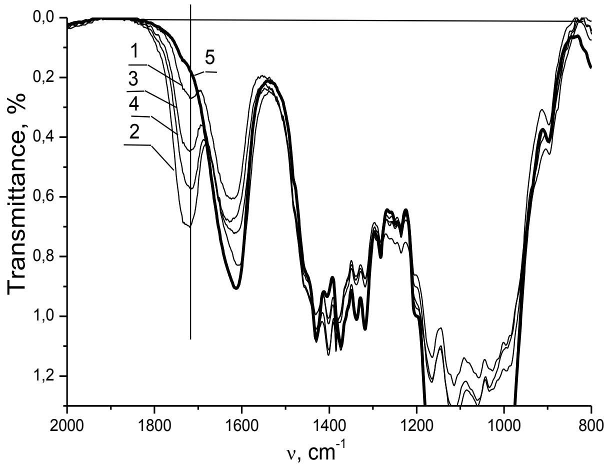


Fig. 2. IR spectra of CNC samples (normalized at 2900 cm^{-1} as a reference band): 1 - CNC (8:2); 2 - CNC (7:3); 3 - CNC (6:4); 4 - CNC (5:5); 5 - CNC (H_2SO_4)

Рис. 2. ИК спектры образцов НКЦ (нормализованы по полосе 2900 см$^{-1}$): 1 - НКЦ (8:2); 2 - НКЦ (7:3); 3 - НКЦ (6:4); 4 - НКЦ (5:5); 5 - НКЦ (H_2SO_4)

The IR spectra of the CNC samples demonstrate absorption bands typical of cellulose. Broad intensive absorption band in a region of 3000-3700 cm^{-1} characterizes stretching vibrations of the cellulose hydroxyl groups participating in hydrogen bonding. The hydroxyl groups in positions C2, C3 and C6 contribute to the formation of intra- and intermolecular hydrogen bonds. Stretching vibrations of C–H bond in CH_2 and CH groups are in a region of 2800-3000 cm^{-1}. Quite intensive absorption bands at 900 and 1160, 1060 and 1110 cm^{-1} are responsible for C-O-C bending vibrations of glycosidic bond and pyranose cycle, respectively. Production of CNC by the hydrothermal method in a mixture of hydrochloric and nitric acids leads to cellulose oxidation. That is manifested in a significant increase of bands intensity around 1720 cm$^{–1}$ and in a region of 1383-1385 cm$^{–1}$ (stretching vibrations of carboxyl group) (Fig. 2, Table 2).

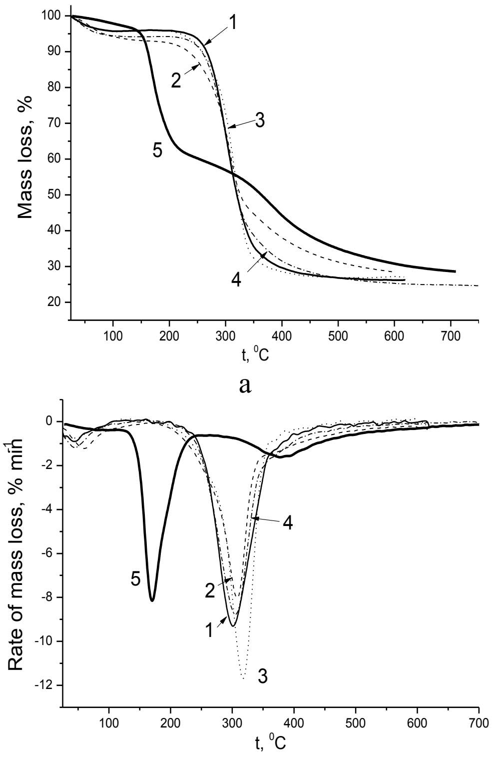
Table 2

The 1720 cm^{-1} band intensities (relative units) in the IR spectra of the CNC samples

***Таблица 2.* Интенсивность полосы 1720 см$^{-1}$ (относительные единицы) в ИК спектрах образцов НКЦ**

	Sample				
	CNC (H_2SO_4)	CNC (8:2)	CNC (7:3)	CNC (6:4)	CNC (5:5)
I_{1720}, normalized at 2900 cm^{-1}	0.161	0.267	0.696	0.447	0.572

Grafting of surface carboxyl groups increases the CNC thermal stability significantly compared to the samples obtained by the standard sulfuric acid hydrolysis. Fig. 3 shows TG and DTG curves for the CNC samples obtained by the standard sulfuric acid hydrolysis and by hydrothermal method in a mixture of HCl and HNO_3.



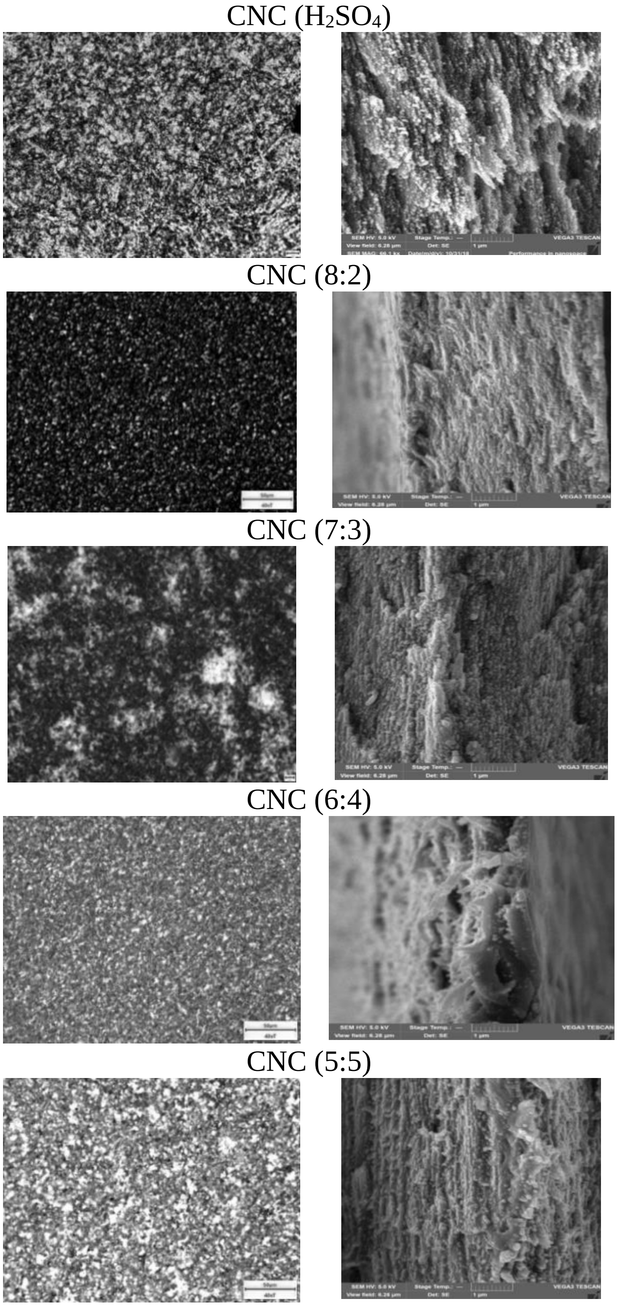
a

b

Fig. 3. TG and DTG curves for the CNC samples obtained by the standard sulfuric acid hydrolysis and under hydrothermal conditions in a mixture of hydrochloric and nitric acids: 1 - CNC (8:2); 2 - CNC (7:3); 3 - CNC (6:4); 4 - CNC (5:5); 5 - CNC (H_2SO_4)

Рис. 3. Кривые ТГ и ДТГ для образцов НКЦ, полученных стандартным сернокислотным гидролизом и в гидротермальных условиях в смеси соляной и азотной кислот: 1 - НКЦ (8:2); 2 - НКЦ (7:3); 3 - НКЦ (6:4); 4 - НКЦ (5:5); 5 - НКЦ (H_2SO_4)

It can be seen (Fig. 3, Table 1) that the temperature of 170 °C, corresponding to the maximum decomposition rate of the sample CNC (H_2SO_4), increases significantly (up to 300-318 °C) for the samples obtained in a mixture of HCl and HNO_3.

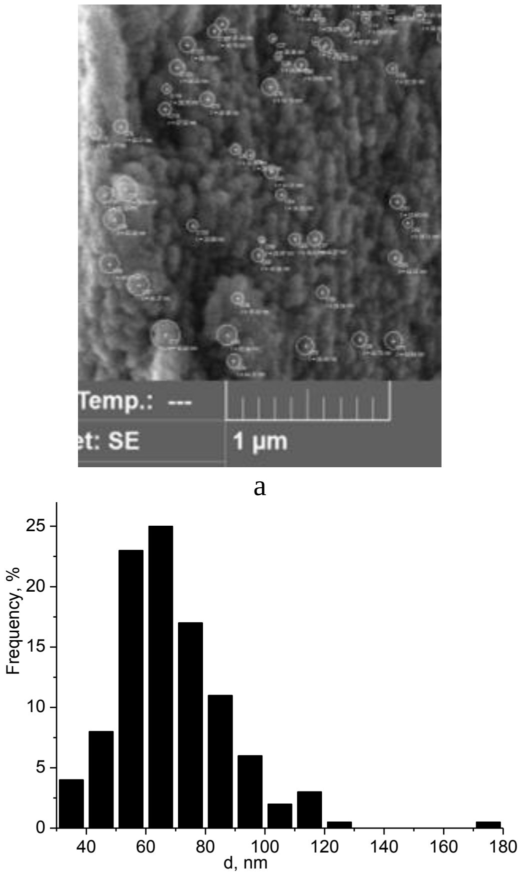


a b

Fig. 4. POM images of the CNC films surface (crossed polarizers, magnification 40 ×) (a); cross-sectional SEM micrographs of the CNC films (scale bar: 1 μm) (b)

Рис. 4. ПОМ изображения поверхности пленок НКЦ (скрещенные поляризаторы, увеличение в 40 раз) (a); СЭМ микрофотографии поперечного сечения пленок НКЦ (масштаб: 1 мкм) (b)

It is worth to note that the CNC samples produced by sulfuric acid hydrolysis show iridescent coloration in a polarized light, unlike the CNC samples obtained by hydrolysis in a mixture of HCl and HNO_3 (Fig. 4, a). The observed interference colors are a consequence of birefringence in the CNC films. The reason for the interference of light is the phase shift caused by difference in refractive indices for polarization along and across the anisotropic rod-like CNC particles obtained by the standard sulfuric acid hydrolysis.



a

b

Fig. 5. SEM image of a cross section of the sample CNC (7:3) for estimating the CNC particles size (scale bar: 1 μm) (a); histogram of particle size distribution for the sample CNC (7: 3) (b)
Рис. 5. СЭМ изображение поперечного сечения образца НКЦ (7:3) для оценки размера частиц НКЦ (масштаб: 1 мкм) (а); гистограмма распределения частиц по размерам для образца НКЦ (7:3) (b)

It has turned out also that under conditions of hydrothermal hydrolysis in a mixture of hydrochloric and nitric acids, shape of the obtained CNC particles is mainly spherical. It is especially evident in the sample CNC (7:3) (Fig. 4, b). Most probably, in the presence of a strong oxidant, hydrolysis occurs not only in amorphous, but also in crystalline regions of cellulose (in part, at the ends of rod-like particles), which affects the final shape of the CNC particles [37, 38].

To estimate the size of spherical CNC particles, a cross-sectional SEM image of the sample CNC (7:3) was used. A sampling of 100 particles was used to plot a bar chart for CNC particle size distribution (Fig. 5). The analysis shows that the average size of the CNC particles is 60-80 nm, which agrees well with the hydrodynamic diameter value (85 nm) obtained by DLS method (Table 1).

CONCLUSIONS

Cellulose nanocrystals (CNC) have been obtained by hydrothermal method in a mixture of hydrochloric and nitric acids at the molar ratios of 8:2, 7:3, 6:4 and 5:5. The CNC yield, particle size, degree of polymerization, temperature of thermal degradation have been determined. Cellulose hydrolysis in a mixture of hydrochloric and nitric acids causes cellulose oxidation to form surface carboxyl groups. A high surface charge determines high colloidal stability of CNC aqueous suspensions. It is found that the CNC particles have a spherical shape with an average size of 60-80 nm. It is noted a significant increase in thermal stability of the CNC samples produced under hydrothermal conditions in a mixture of hydrochloric and nitric acids.

This work was supported by the Russian Foundation for Basic Research (project number 18-43-370004 r_a.).

The authors would like to thank The Upper Volga Region Centre of Physicochemical Research (Ivanovo, Russia) and Centre for collective use of scientific equipment of Ivanovo State University of Chemistry and Technology (Russia) for some measurements carried out using the centers’ equipment.

REFERENCES
ЛИТЕРАТУРА

1. **Rogovin Z.A.** Chemistry of cellulose. M.: Khimiya. 1972. 520 p. (in Russian). **Роговин З.А.** Химия целлюлозы. М.: Химия. 1972. 520 с.
2. **Bikales N.M., Segal L.** Cellulose and cellulose derivatives. N.-Y.: Wiley. 1971. 501 p.
3. **Rogovin Z.A., Gal'braikh L.S.** Chemical transformations and modification of cellulose. M.: Khimiya. 1979. 208 p. (in Russian). **Роговин З.А., Гальбрайх Л.С.** Химические превращения и модификация целлюлозы. М.: Химия. 1979. 208 с.
4. **Panov V.P., Zhbankov R.G.** Intra- and intermolecular interactions in carbohydrates: (Non-valent interactions and conformations). Minsk: Nauka i tekhnika. 1988. 356 p. (in Russian). **Панов В.П., Жбанков Р.Г.** Внутри- и межмолекулярные взаимодействия в углеводах (невалентные взаимодействия и конформации). Минск: Наука и техника. 1988. 356 с.
5. **Udoratina E.V., Torlopov M.A.** Partial destruction of cellulose in water and in acetic acid in presence of heteropolyacids. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2013. V. 56. N 6. P. 69-75 (in Russian). **Удоратина Е.В., Торлопов М.А.** Частичная деструкция целлюлозы в воде и в уксусной кислоте в присутствии гетерополикислот. *Изв. вузов. Химия и хим. технология.* 2013. Т. 56. Вып. 6. С. 69-75.
6. **Surov O.V., Voronova M.I., Rubleva N.V., Kuzmicheva L.A., Nikitin D., Choukourov A., Titov V.A., Zakharov A.G.** A novel effective approach of nanocrystalline cellulose production: oxidation–hydrolysis strategy. *Cellulose*. 2018. V. 25. N 9. P. 5035–5048. DOI: 10.1007/s10570-018-1910-4.
7. **Moon R.J., Martini A., Nairn J., Simonsen J., Youngblood J.** Cellulose nanomaterials review: structure, properties and nanocomposites. *Chem. Soc. Rev.* 2011. V. 40. N 7. P. 3941-3994. DOI: 10.1039/C0CS00108B.

8. **Giese M., Blusch L.K., Khan M.K., MacLachlan M.J.** Functional Materials from Cellulose-Derived Liquid-Crystal Templates. *Angew. Chem. Int. Ed.* 2015. V. 54. N 10. P. 2888-2910. DOI: 10.1002/anie.201407141.
9. **Zhu H., Wei Luo W., Ciesielski P.N., Fang Z., Zhu J.Y., Henriksson G., Himmel M.E., Hu L.** Wood-Derived Materials for Green Electronics, Biological Devices, and Energy Applications. *Chem. Rev.* 2016. V. 116. N 16. P. 9305–9374. DOI: 10.1021/acs.chemrev.6b00225.
10. **Surov O.V., Voronova M.I., Zakharov A.G.** Functional materials based on nanocrystalline cellulose. *Russ. Chem. Rev*. 2017. V. 86. N 10. P. 907–933. DOI: 10.1070/RCR4745.
11. **Hamad W.Y., Hu T.Q.** Structure–process–yield interrelations in nanocrystalline cellulose extraction. *Can. J. Chem. Eng.* 2010. V. 88. N 3. P. 392-402. DOI: 10.1002/cjce.20298.
12. **Lin N., Dufresne A.** Surface chemistry, morphological analysis and properties of cellulose nanocrystals with gradiented sulfation degrees. *Nanoscale*. 2014. V. 6. N 10. P. 5384–5393. DOI: 10.1039/C3NR06761K.
13. **Voronova M.I., Surov O.V., Zakharov A.G.** Nanocrystalline cellulose with various contents of sulfate groups. *Carbohyd. Polym*. 2013. V. 98. N 1. P. 465–469. DOI: 10.1016/j.carbpol.2013.06.004.
14. **Yu H.Y., Qin Z.Y., Liang B.L., Liu N., Zhou Z., Chen L.** Facile extraction of thermally stable cellulose nanocrystals with a high yield of 93% through hydrochloric acid hydrolysis under hydrothermal conditions. *J. Mater. Chem. A.* 2013. V. 1. N 12. P. 3938–3944. DOI: 10.1039/C3TA01150J.
15. **Camarero Espinosa S., Kuhnt T., Foster E.J., Weder C.** Isolation of thermally stable cellulose nanocrystals by phosphoric acid hydrolysis. *Biomacromolecules*. 2013. V. 14. N 4. P. 1223–1230. DOI: 10.1021/bm400219u.
16. **Hamid S.B.A., Zain S.K., Das R., Centi G.** Synergic effect of tungstophosphoric acid and sonication for rapid synthesis of crystalline nanocellulose. *Carbohydr. Polym.* 2016. V. 138. P. 349–355. DOI: 10.1016/j.carbpol.2015.10.023.
17. **Jonoobi M., Oladi R., Davoudpour Y., Oksman K., Dufresne A., Hamzeh Y., Davoodi R.** Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: a review. *Cellulose.* 2015. V. 22. N 2. P. 935–969. DOI: 10.1007/s10570-015-0551-0.
18. **Chen G.Y., Yu H.Y., Zhang C.H., Zhou Y., Yao J.M.** A universal route for the simultaneous extraction and functionalization of cellulose nanocrystals from industrial and agricultural celluloses. *J. Nanopart. Res.* 2016. V. 18. N 2. P. 1–14. DOI: 10.1007/s11051-016-3355-8.
19. **Chen L., Zhu J.Y., Baez C., Kitin P., Elder T.** Highly thermal-stable and functional cellulose nanocrystals and nanofibrils produced using fully recyclable organic acids. *Green Chem.* 2016. V. 18. N 13. P. 3835–3843. DOI: 10.1039/C6GC00687F.
20. **Yu H.Y., Zhang D.Z., Lu F.F., Yao J.** New approach for single - step extraction of carboxylated cellulose nanocrystals for their use as adsorbents and flocculants. *ACS Sustain. Chem. Eng.* 2016. V. 4. N 5. P. 2632–2643. DOI: 10.1021/acssuschemeng.6b00126.
21. **Titova Yu.V., Voronova M.I., Maksimov A.I.** Influence of gas-discharge plasma treatment in the electrolyte bulk on the cellulose properties. *Russ. J. Appl. Chem.* 008. V. 81. N 5. P. 854–857. DOI: 10.1134/s107042720805025x.
22. **Zhang K., Sun P., Liu H., Shang S., Song J., Wang D.** Extraction and comparison of carboxylated cellulose nanocrystals from bleached sugarcane bagasse pulp using two different oxidation methods. *Carbohydr. Polym.* 2016. V. 138. P. 237–243. DOI: 10.1016/j.carbpol.2015.11.038.
23. **Cheng M., Qin Z.Y., Liu Y.N., Qin Y.F., Li T., Chen L., Zhu M.F.** Efficient extraction of carboxylated spherical cellulose nanocrystals with narrow distribution through hydrolysis of lyocell fibers by using ammonium persulfate as an oxidant. *J. Mater. Chem. A.* 2014. V. 2. N 1. P. 251–258. DOI: 10.1039/C3TA13653A.
24. **Kumar V., Yang T.** HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation of cellulose—preparation and characterization of bioabsorbable oxidized celluloses in high yields and with different levels of oxidation. *Carbohydr. Polym.* 2002. V. 48. N 4. P. 403–412. DOI: 10.1016/S0144-8617(01)00290-9.
25. **Xu Y.H., Liu X., Liu X., Tan J.L., Zhu H.L.** Influence of HNO_3/H_3PO_4–$NaNO_2$ mediated oxidation on the structure and properties of cellulose fibers. *Carbohydr. Polym.* 2014. V. 111. P. 955–963. DOI: 10.1016/j.carbpol.2014.05.029.
26. **Leung A.C., Hrapovic S., Lam E., Liu Y., Male K.B., Mahmoud K.A., Luong J.H.** Characteristics and properties of carboxylated cellulose nanocrystals prepared from a novel one-step procedure. *Small.* 2011. V. 7. N 3. P. 302–305. DOI: 10.1002/smll.201001715.
27. **Cheng M., Qin Z., Chen Y., Liu J., Ren Z.** Facile one-step extraction and oxidative carboxylation of cellulose nanocrystals through hydrothermal reaction by using mixed inorganic acids. *Cellulose.* 2017. V. 24. N 8. P. 3243–3254. DOI: 10.1007/s10570-017-1339-1.
28. **Beck S., Bouchard J., Berry R.** Dispersibility in Water of Dried Nanocrystalline Cellulose. *Biomacromolecules*. 2012. V. 13. N 5. P. 1486–1494. DOI: 10.1021/bm300191k.
29. **Boluk Y., Danumah C.** Analysis of cellulose nanocrystal rod lengths by dynamic light scattering and electron microscopy. *J. Nanopart. Res.* 2014. V. 16. N 1. P. 2174. DOI: 10.1007/s11051-013-2174-4.
30. **Brinkmann A., Chen M., Couillard M., Jakubek Z.J., Leng T., Johnston L.J.** Correlating Cellulose Nanocrystal Particle Size and Surface Area. *Langmuir*. 2016. V. 32. N 24. P. 6105–6114. DOI: 10.1021/acs.langmuir.6b01376.
31. **Beuguel Q., Tavares J.R., Carreau P.J., Heuzey M.-C.** Ultrasonication of spray- and freeze-dried cellulose nanocrystals in water. *J. Colloid Interf. Sci.* 2018. V. 516. P. 23–33. DOI: 10.1016/j.jcis.2018.01.035.
32. **Ioelovich M., Leykin A.** Nano-cellulose and its applications. *Sci. Israel – Technolog. Advant.* 2004. V. 6. N 3-4. P. 17-25.
33. **Hamad W.Y., Hu T.Q.** Structure–Process–Yield Interrelations in Nanocrystalline Cellulose Extraction. *Can. J. Chem. Eng.* 2010. V. 88. N 3. P. 392-402. DOI: 10.1002/cjce.20298.
34. **Yu H., Qin Z., Liang B., Liu N., Zhou Z., Chen L.** Facile extraction of thermally stable cellulose nanocrystals with a high yield of 93% through hydrochloric acid hydrolysis under hydrothermal conditions. *J. Mater. Chem. A.* 2013. V. 1. P. 3938–3944. DOI: 10.1039/c3ta01150j.
35. **Kontturi E., Meriluoto A., Penttilä P.A., Baccile N., Malho J.-M., Potthast A., Rosenau T., Ruokolainen J., Serimaa R., Laine J., Sixta H.** Degradation and Crystallization of Cellulose in Hydrogen Chloride Vapor for High-Yield Isolation of Cellulose Nanocrystals. *Angew. Chem. Int. Ed.* 2016. V. 55. P. 14455 –14458. DOI: 10.1002/anie.201606626.
36. **Lorenz M., Sattler S., Reza M., Bismarck A., Kontturi E.** Cellulose nanocrystals by acid vapour: towards more effortless isolation of cellulose nanocrystals. *Faraday Discuss*. 2017. V. 202. P. 315–330. DOI: 10.1039/c7fd00053g.
37. **Wang N., Ding E., Cheng R.** Preparation and Liquid Crystalline Properties of Spherical Cellulose Nanocrystals. *Langmuir*. 2008. V. 24. N 1. P. 5-8. DOI: 0.1021/la702923w.
38. **Xiong R., Zhang X., Tian D., Zhou Z., Lu C.** Comparing microcrystalline with spherical nanocrystalline cellulose from waste cotton fabrics. *Cellulose.* 2012. V. 19. N 4. P.1189–1198. DOI: 10.1007/s10570-012-9730-4.

Поступила в редакцию (Received) 25.01.2019
Принята к опубликованию (Accepted) 12.11.2019