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Structures and prproperties of nanocellulose

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ABSTRACT

In this paper the possibility of influence cotton cellulose acid hydrolysis conditions to nanocelluloses properties, structure and dimension was investigated. Nanocellulose whiskers (50-300x10-40 nm) and balls (50-300 nm) are synthesized by depending on different conditions of reaction. By methods of X-ray diffraction, infrared spectroscopy and TEM, SEM, AFM microscopies were studied physico-chemical properties and structure of nanocellulose. It is shown the possibility of biodegradation and resorption of nanocellulose by injection into animal's skin.

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KEYWORDS

Nanocellulose;
Microcrystalline cellulose;
Cotton cellulose;
Acid hydrolyze;
Formation.

INTRODUCTION

Preparation and formation of cellulose nanoparticles and study their structures and properties by physic-chemical and physical methods, has shown obvious scientific interest.

It is occurred the irreversible changes of physic-chemical and exploitation properties by decreasing size of cellulose particles under the influence of chemical, physical and mechanical factors. Except that, considerably increasing their reaction activity, swelling capacity, quantity of reactivity functional groups and etc.

Changes of physico-chemical and performance specification of cellulose particles, by conversion from microsize to nanosize, will promote expansion of their application spheres and creation of new materials with unique properties.

Nanocellulose (NC) is a new class of deriva-

tive cellulose that characterized by high crystalline, high developed surface, improved ability of dispersion and ability to degradable by microorganisms and so on^[1-3].

Cellulose is the most widespread renewed natural organic polymer. The most valuable source of cellulose is cotton that contains till 95 % pure cellulose. The investigation structure of cotton fibers and cellulose based on to supramolecular level allow to explaining mechanisms of physical and chemical modification of cellulosic.

The supramolecular structure of cotton fiber was topic of numerous researches, in results its basic characteristics right up to structure with correspondingly model were study sufficiently^[4,5,6]. It was found that the surface of cotton fiber consists of cuticle - an unstructured cover in the thickness 500 Å. The primary wall of fiber is formed by fibrillar grids with the thickness 500-1000 Å. The first layer of

secondary wall is formed from densely packed by fibrillar bunches located under the relation of an axis of fiber at an angle from 40-60° and has thickness about 0,1 microns. The secondary wall is the main part of fiber on volume and consists from microfibrill twirled on spiral round fiber, that angle of slope amount to 25-30°, and approached to the central canals of fiber, the angle of slope amount to 5°. The layer of microfibrillis formed from lamellae with thickness 0,1-0,2 microns. The third wall of fiber consists of the remainder of protoplasm with thickness 0,1 microns. The form of central tunnels of fiber is partially gyrate ellipse in length 3-5 microns and width 0,3 - 0,6 microns. At cellulose the nanoparticles and nanostructures are formed in result of selforganising of macromolecules during processes of its biosynthesis, modification and destruction.

For cotton fibers and celluloses based on it is significant that amorphously - crystal structure. Crystalline and amorphous parts don't have clear boundary and transition from the ordered crystal parts to less ordered amorphous part occurs gradually and average degree crystallinity cellulose amount to 63-67 %.

The aim investigation was study structure and properties of NC, obtained from cotton cellulose by chemical and physical methods.

EXPERIMENTAL

Hydrolysis of cotton cellulose was carried out by 10-62 % aqueous solution of sulfuric acid at temperature 25-100 °C for from 2 minutes till 24 hours.

Ultrasonic dispersion (USD) was performed at frequency of 35 KHz for 5-60 minutes at ultrasonic instrument model UZDN -1 V - 4.2. Microwaves (MW) were performed at microwave instrument model MDS- 282 at 2450 MHz frequency.

IR - spectroscopic investigations were performed by instruments model "Specord -75IR" and DRON -3M diffractometer was used for X-ray investigation, shape and size of particles were determined by electron microscope TEM – 100, scanning electron microscope SEM-200 and atomic force microscope model Aligent 5500.

RESULTS AND DISCUSSION

Selection water as environment for hydrolysis cellulose could be explained, that it possesses high plasticize ability. Cellulose swells in water, at the expense of its high penetrating ability on macro- and microcracks and central tunnel of fiber. It is known that hydrolytic destruction intensity of cotton cellulose depends on temperature, time of hydrolysis and concentration of acid.

It is established that at hydrolysis of cotton cellulose by 10 % - aqueous solution of sulfuric acid the specified changes are shown after 10-12 minutes at temperature of boiling of hydrolyzing solution than at concentration 62 % - aqueous solution of acid, they hydrolyzed after 2 minutes. Increasing time of hydrolysis of cellulose at 10 % - aqueous solution of sulfuric acid at 25°C till 24 hours and more practically doesn't influence to size crystallites. It is occurred lateral splitting up of fiber at the expense of solubilization and removal of less ordered parts of lamellae with formation of microcrystalline cellulose (MCC) with 71-72 % degree of crystallinity. Thus practically doesn't occur longitudinal splitting up of fibrils and their diameter stays unchanged in range 15-20 microns at the average size in length 80-120 microns.

It is possible to decrease the average size of particles till 10-40 micron by UZD treatment, at the expense of splitting up particles of MCC by micro- and macro- break which has been shown by microscopic investigations.

At hydrolysis of cellulose with sulfuric acid at concentration 62% by 25°C temperature, crystallites considerably swell, their form destroyed and occur further lateral destruction to more smaller crystallite, that allows to assume that in system cellulose - water - acid, concentration of sulfuric acid above 62 % become critical.

The average size of particles may decrease till nanosize by using USD at the expense of splitting of particles MCC on micro- and macrocracks, which has been formed at MW processing (Figure 1).

X-ray investigations have shown that for NC, at considered interval of angle dispersion against amorphous halo has three crystal maximum. The most in-

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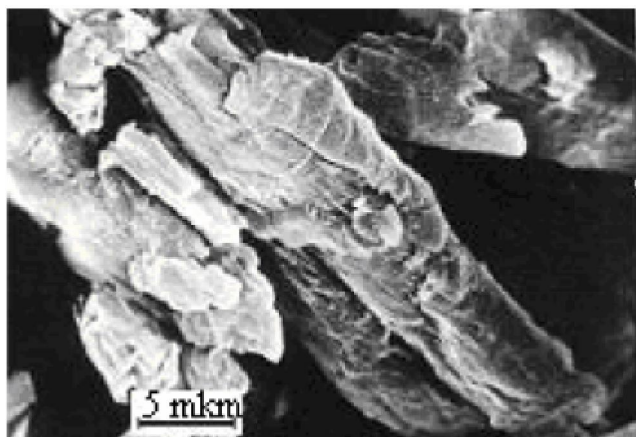


Figure 1 : SEM - images of MCC

tensive maximum observing at value of angle $2\theta = 22.5 - 22.6^\circ$ belong to crystallographic reflex (002). At result of mathematical processing it has been established that the narrowest peak 1 belong to linear part of macromolecules of cellulose, the peak 2 belong to the deformed (bent) molecules, and the wide peak 3 belong to amorphous cellulose.

Except specified maximum peaks are observed also partially over each other with indexes (101) and (10-1) which arrange at angle $15-16.5^\circ$. Cristalphysical calculations gives next sizes of interplanar spacing: $d_{101}=0,591$ nm, $d_{10-1}=0,537$ nm, $d_{002}=0,391$ nm (TABLE 1). On the base of X-ray diffraction width (10-40 nm) and length (50-300 nm) elementary crystallites of NC.

According to X-ray investigation in range of concentration H_2SO_4 10-62 %, obtained of NC particles are kept 75-81 % degree crystalline.

The further increasing of concentration of acid more critical concentration bring to decrease of degree crystallinity till 25 %. Probably at high concentration of acid start rupture of intermolecular bond between fibrils of cellulose that bring to destruction crystallites of cellulose. At acid concentration more than 62 % formed particles move to hydrolyzing solution, due to deeply hydrolysis till oligomers and solutions become transparent.

TABLE 1 : The structural parameters of nanocellulose

Parameters	Crystalline reflex			
	101	10-1	002	040
Location maximum 2θ , (deg.)	14.75	16.25	22.7	34.5
Interdimensional interval d , (Å)	5.91	5.37	3.91	2.6
Width peak on 0.5 altitude β , (rad.)	0.0209	0.0209	0.0235	0.0244
Size of crystalline particle l , (Å)	67.71	67.83	60.90	60.21
Degree of crystallinity (on intensity 002)			0.96	
Degree of crystallinity (on area)			0.81	
Thickness amorphous seam, (Å)			15.05	
Wide period L , (Å)			79.21	

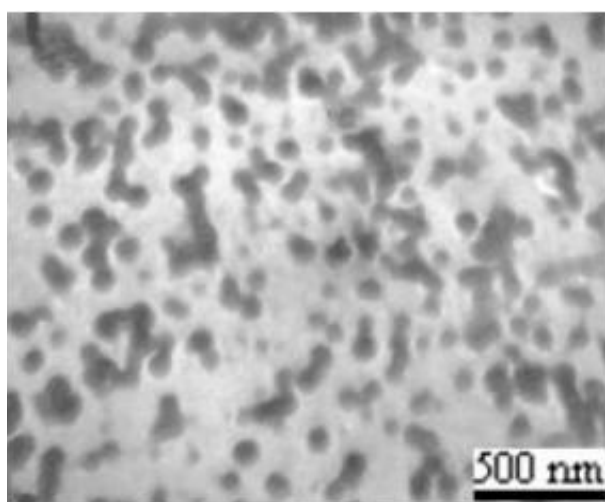
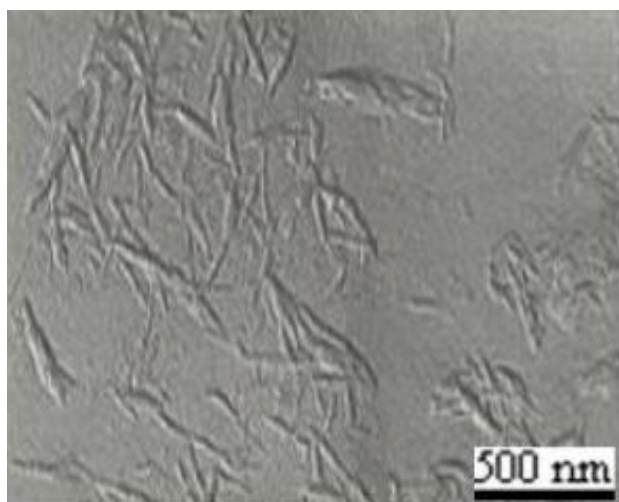


Figure 2 : TEM picture samples of nanocellulose whiskers (a) and balls (b)

The NC obtained at relatively the low concentration of acid < 50% and temperatures < 50°C, at consequent their processing in MW and USD has rod-like structure (whiskers) with sizes 50-300x10-40 nm (Figure 2a) and nanocrystallites stay unimpaired. At increasing concentration of acid hydrolysis process is accompanied by reduction of the sizes of particles with simultaneous depolymerization macromolecules of cellulose and decrease in an efficiency of final product. If the concentration of $H_2SO_4 > 50\%$ and temperature > 50 °C than, NC has ellipsoidal (spherical) forms (balls) with wide distribution in size (Figure 2b).

AFM investigations has shown that the NC form and size range at the wide diapason that connected with processes of NC particles agglomeration. It is detection, that the NC with the rod-like (whiskers) form has dimension from 82 till 164 nm.

By IR spectroscopic investigation it has shown

that spectra's of NC are typical for cotton cellulose, however, intensity of peaks higher (Figure 4).

NC gels have micelle structure and are aggregative unstable system, can't keep without the stabilizer a constancy micellaric concentration. Process adhesion particles are spontaneous irreversible process. Formations of agglomerates at concentration NC have been found by AFM - investigations.

It is investigated possibility prevention of agglomeration process of NC particles by obtaining their polymer-polymeric mixing. Obtained high disperse systems could be prevent from adhesion particles of disperse phase⁽⁷⁾.

At NC gels surface of particles should have border of section of two phases «water - NC» where formed adsorptive layers. These layers can be formed by molecules of the third component on surface of NC particles. But thus the great value has

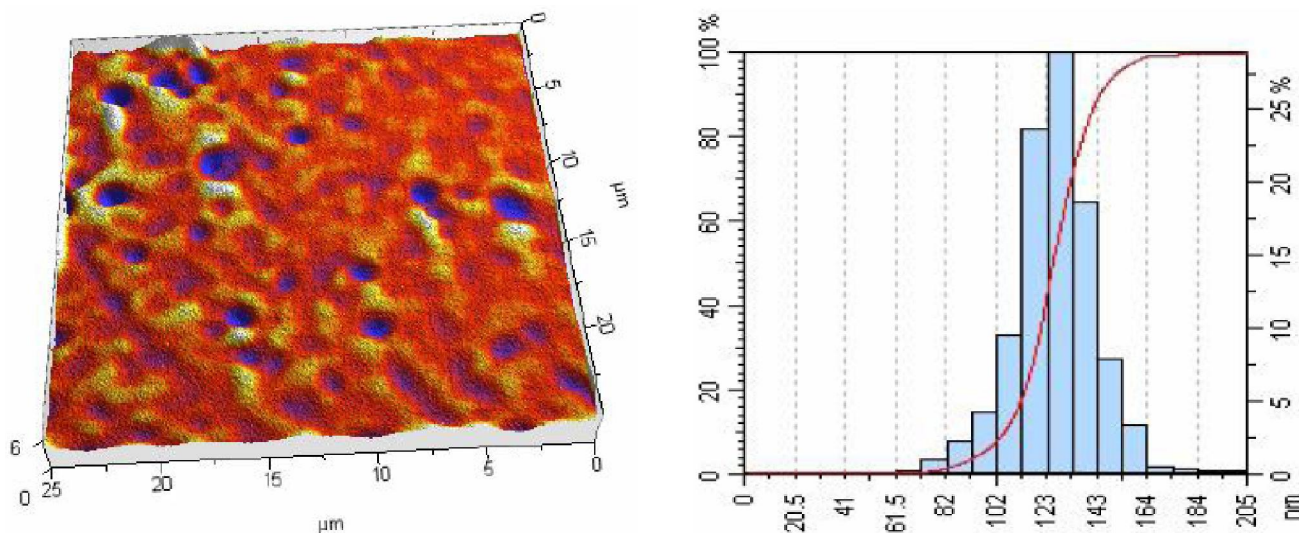


Figure 3 : AFM image of NC and distribution at sizes

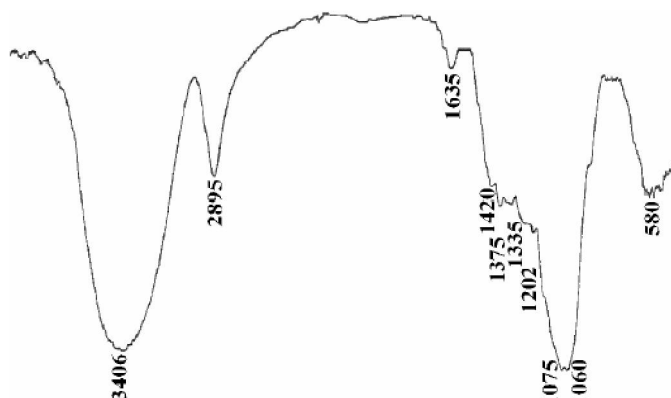


Figure 4 : IR-spectra of NC

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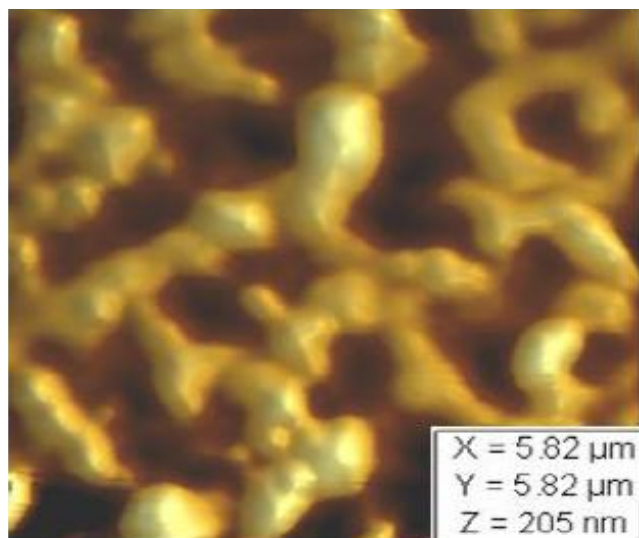


Figure 5 : AFM - images of NC

character of orientation molecules of the third component in adsorptive layer. The maximum stability of system was obtained at formation of full monomolecular layer.

For the stabilization nanocrystallites has chosen Na-carboxymethylcellulose (CMC), which the most near on NC content and structure.

At addition CMC solution to NC gel, on surface of swelling to NC particles are formed negatively charged protecting agent. The cover from hydrogenate ionogenic groups of diffusion layer of CMC around colloidal NC particles is a protecting

agent of NC particles from agglomeration and reason of aggregate stability of hydrogels^[8].

Investigation of influence of concentration water solutions of CMC to process of agglomeration of NC particles has shown that it can be prevent, by adding diluted solution of CMC to hydrogel of NC with concentration 0,03÷0,05 %.

It is experimentally established that, NC samples at diluted CMC solutions doesn't become syneresis at their keep from six till eighteen months, it could be explain that, apparently to prevention process of agglomeration of NC particles due to formation micellar capsule round each particle from interrepulsion negatively charged covers by macromolecules of CMC.

Dispersed particles of NC in the solution CMC with various concentration has been done precipitate by acetone and dried at temperature $40 \pm 2^\circ\text{C}$.

Thus it is established that at concentration 0,03÷0,05 % of solutions Na-CMC the precipitate and dried up of samples NCC at repeated immersing in water the form stable hydrogel compositions and doesn't become to agglomerate.

It is definitely established that by entering of cellulose and MCC to skin of animal and intramuscularly during some time they don't become to biodegradable and resolve.

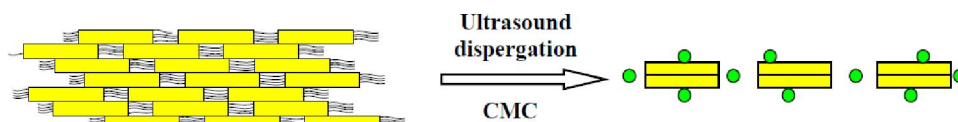


Figure 6 : Assumed scheme of stabilization NC particles

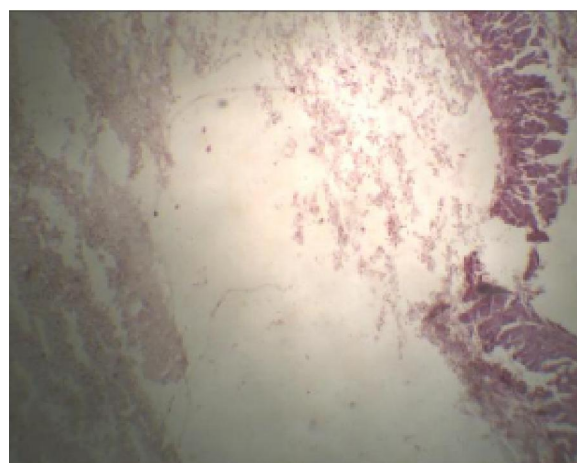
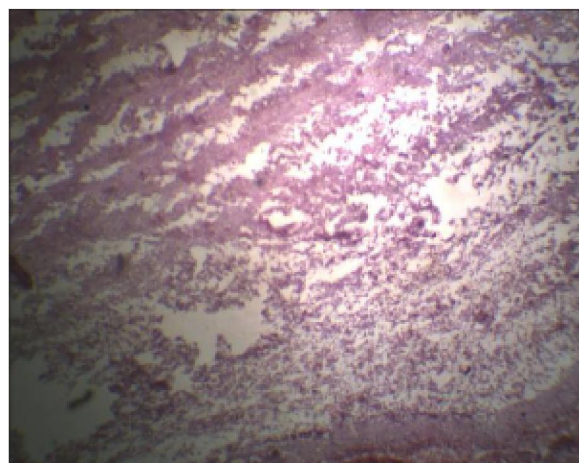


Figure 7 : TEM-images of ultrafine section cells rats at time; a - after 1-day injection; b - after 30 - days injection.

For this aim we had been investigated possibility of biodegradation of NC in organism and were carried out medico-biological tests.

Animal single injection was carry out, by 1 % water sterile suspensions of NC hypodermically in the field of back between shovels and buttocks. The condition and character of tissue reaction of muscles wall and hypodermic cellular have been studied.

TEM investigation have shown that, NC homogeneous, has roundish form after 1 day injection, become painted in pink colour, the initial stages edge resorption (Figure 7a) are visible. After 30 days on animals tissues presence of NC doesn't founded and during investigation hasn't been situation of lethal outcome of white rats even after 6 months.

CONCLUSIONS

Thus, influence of condition of obtained NC on its properties and structures were investigated.

It was found that at mild conditions with using of physical factors (USD, MW) obtained NC has rod-like shape (whiskers) with sizes 50-300x10-40 nm with high degree of crystallinity and yield than harsh environment of hydrolysis are bring to obtain NC like spherical shape (balls) with sizes by 50-300 nm with less yield and degree of crystallinity.

It has shown the possibility of biodegradable and resorption of NC at hypodermic injection of animal.

Consequently, it could be assume that, on the basis NC could be make new type of biologically active prolongate preparations with new unique properties, in particular, biodegradabled polymeric drugs and medical goods, possessing in advance assigned exploitation properties.

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