

18. Cibul's'ka, L. V. Multifunctional additive based on the 5-amino-1,2,4-dithiazole-3-thione [Text] / L. V. Cibul's'ka, I. M. Vasil'kevich, V. V. Filinova. – Mastil'ni materiali, 1997. – 182 p.
19. Pat. USA 3862942. Preparation of 2,4,6-tris(hydroxybenzylthio)triazines [Text] / Grilles J. – Ref. J. Chem, 1975. – 22H243.
20. Sanin, P. I. Installation for the oxidation of organic liquids with the automatic compensation and registration of consumable oxygen [Text] / P. I. Sanin, L. F. Chernjavs'kaja, V. V. Sher // Neftehimija. – 1966. – Vol. 6. – P. 112–114.

Досліджено різні стадії обробки волокон конопель у процесі одержання мікрокристалічної целюлози. Визначено оптимальні умови проведення лужної екстракції волокон конопель, органосольвентного варіння, хелатування і гідролізу целюлози. Встановлено, що проведення вказаних стадій обробки за оптимальних значень технологічних параметрів призводить до отримання мікрокристалічної целюлози, яка за вмістом сульфатної золи і ступенем полімеризації відповідає вимогам стандарту

Ключові слова: мікрокристалічна целюлоза, волокно конопель, екстракція, гідроліз, рентгенівська дифракція, термогравіметричний аналіз

Исследованы различные стадии обработки волокон конопли в процессе получения микрокристаллической целлюлозы. Определены оптимальные условия проведения щелочной экстракции волокон конопли, органосольвентной варки, хелатирования и гидролиза целлюлозы. Установлено, что проведение указанных стадий обработки при оптимальных значениях технологических параметров приводит к получению микрокристаллической целлюлозы, которая по содержанию сульфатной золи и степени полимеризации соответствует требованиям стандарта

Ключевые слова: микрокристаллическая целлюлоза, волокно конопли, экстракция, гидролиз, рентгеновская дифракция, термогравиметрический анализ

UDC 676.166+661.123

DOI: 10.15587/1729-4061.2016.71275

DEVELOPMENT THE TECHNOLOGY OF OBTAINING MICROCRYSTALLINE CELLULOSE FROM THE HEMP FIBERS

V. Barbash

PhD, Associate Professor*

E-mail: v.barbash@kpi.ua

M. Karakutsa*

E-mail: mary-skies@yandex.ua

I. Trembus

PhD, Associate Professor*

E-mail: lanos0790@yandex.ru

O. Yaschenko

Postgraduate Student*

E-mail: volia@ukr.net

*Department of ecology and plant polymer technologies
National Technical University of Ukraine
"Kyiv Polytechnic Institute"
Peremohy ave., 37, Kyiv, Ukraine, 03056

1. Introduction

The number of studies of new promising materials based on natural polymers has increased significantly lately, in particular cellulose, which is related to economic and ecological necessity of replacing natural exhaustible sources of carbohydrates (oil, coal) to renewable plant raw materials. Due to its valuable properties, cellulose successfully finds its application not only in paper industry but in other industrial areas, such as chemical, food, pharmaceutical, cosmetic. One of the most promising products of cellulose chemical processing is the microcrystalline cellulose (MCC), which has high content of the ordered part of cellulose with crystallographic orientation of the macromolecules [1, 2], the maximum degree of crystallinity, high density and specific surface [3].

MCC is characterized by chemical resistance, insolubility in water and organic solvents, absence of taste, smell and

color that allow using it as a filler, stabilizer and emulsifier in food processing, cosmetic and pharmaceutical industries [4].

The main raw material for obtaining microcrystalline cellulose remains high-quality cellulose produced from wood and cotton. The countries that have no available stocks of wood and cotton as the resources of fibers for obtaining MCC, can consider non-wood plant raw materials, such as bast plants, which have more homogeneous long cells, such as fibers of flax, hemp, kenaf [5].

One of the most profitable crops among those plants in Ukraine remains hemp. Favorable weather conditions, a large reserve of fertile lands, existing human and industrial potential promote the cultivation of hemp in Ukraine. Taking into account that a hectare of hemp produces the weight gain of 6 m³ per year, while deciduous trees do only up to 3.2 m³, the change of wood to hemp during the processing of cellulose is considered advisable economically and ecologically as well [6].

2. Analysis of scientific literature and the problem statement

There are different methods of MCC obtaining to provide a required complex of its properties, such as mechanical (grinding), thermo-mechanical, chemical (hydrolysis), precipitation the cellulose from the solution in a powder form [7]. The majority of methods of MCC obtaining in the industry are based on the effect of different chemical reagents on the prepared beforehand plant raw materials that provide the transfer of the bulk of lignin, hemicelluloses, extractive and mineral substances to the solution. Cellulose indexes obtained as a result of chemical treatment, depend on the quantity and sequence of stages of MCC obtaining, the values of their technological parameters, the type of plant raw materials and chemical reagents used in the process of its manufacturing. The majority of existing industrial chemical methods of MCC obtaining are characterized by pollution of the environment, associated with the use of environmentally harmful chemicals, including sulfuric and chlorine-containing reagents [8].

In industrial conditions, MCC is obtained mostly by the chemical method, particularly by hydrolysis of technical cellulose with solutions of various chemicals (acids, alkalis, salts, acidic peroxide) that can destroy the structure of the cell's wall [4, 9]. During such a processing, the partial destruction of lignin and hemicelluloses occurs, as well as the partial destruction of the cellulose macromolecules with the removal of the amorphous fraction, which helps to increase specific surface and sorption properties of MCC relative to the original raw material [7].

The classic method to obtain MCC is considered to be in the form of white powder with the help of hydrolysis of natural or technical cellulose with 2.5 n. hydrochloric acid at 105 °C to form cellulose with a degree of polymerization [10].

To reduce the ecological load on the environment, in recent years organic solvent methods of obtaining cellulose have been actively developed, in particular using the solutions of hydrogen peroxide and acetic acid [11]. The known method of obtaining cellulose of low-ash raw materials (straw and rice husks), which includes preliminary alkali extraction with further oxidative organosolv cooking by the solution of peracetic and acetic acids and hydrogen peroxide in various ratios [12].

In earlier papers [13–15], the influence of preliminary alkaline and acid processing of flax and hemp fibers on cellulose indexes was studied and it was shown that the increased content of mineral substances in fibers of non-wood plant raw materials, compared to wood raw materials, creates the necessity to carry out additional stages of processing to reduce the ash content in MCC to the level of the standard requirements. However, the designed technological modes require further study of the conditions of various stages of hemp fibers treatment and determining optimal technological parameters of obtaining microcrystalline cellulose [16].

3. The purpose and objectives of the study

The aim of this work is to develop technology obtaining of microcrystalline cellulose from fibers of the hemp, which is suitable for use in the pharmaceutical industry.

To achieve the specified goal, the following tasks are set:

– to study the influence of the main technological parameters (concentration of reagents, temperature, duration)

of various stages of the hemp fibres treatment on the indexes of quality of the obtained pulps;

– to analyze the changes of structural characteristics of pulps from hemp fibers by physical and chemical methods of research.

4. Materials and methods of the research of the process of obtaining microcrystalline cellulose from hemp fibers

To obtain microcrystalline cellulose, in this paper we studied the hemp fibers of the 2012 crop from Chernigov Region (Ukraine), which had the following chemical composition: cellulose – 46.2 %; lignin – 17.0 %; resins, fats, waxes – 1.4 %; pentosans – 20.2 %; ash – 1.44 %; sulfate ash – 1.63 % to the weight of absolutely dry raw material (a. d. m.).

Fibers of hemp were separated from impurities (scutch, leaves, grass), ground to the size of 3...5 mm and stored in exiccators to maintain constant humidity and chemical composition. The volume of scutch in the fibers of hemp did not exceed 5 %.

To reduce the content of mineral substances, we carried out preliminary extraction of the ground fibers of hemp with KOH solutions of different concentrations. To do this, the samples of ground fibers were placed in the heat-resistant conic flasks, added with a solution of required concentration and the flasks were connected with reverse refrigerators. To provide the process temperature of 95±2 °C, the flasks were installed on the water bath. Alkali extraction was carried out during 30...240 min, concentration of KOH solution was 3, 5 and 7 % and liquid-to-solid ratio 10:1. After the end of the processing, pulp was rinsed with distilled water to neutral pH, dried in the open air and the quality indexes of the pulp were identified according to standard methods [16].

On the second stage of hemp pulp treatment, we carried out the cooking process of of hemp pulp in a mixture of formic acid and H₂O₂ in the ratio 40:60, 50:50 and 60:40 of volume % at liquid-to-solid ratio 10:1, at temperature of 100 °C during 60 ...210 min. The cooking process was carried out in a heat-resistant conic flasks installed on asbestos grids and connected with reverse refrigerators. After the end of the cooking, the cellulose was rinsed with distilled water to a neutral reaction, dried in the open air and the quality indexes of the pulp were identified.

Chelation of obtained cellulose was carried out with a solution of trilon B with concentration 10 g/l with consumption of 10 % to the weight of a. d. m. during 30 min. under conditions that are taken on the basis of the previous research [15].

To reduce the residual content of mineral substances and the degree of polymerization of hemp MCC, hydrolysis by the solution of CH₂COOH and H₂O₂ in the ratio 50:50 during 90, 120 and 150 min. at liquid-to-solid ratio 10:1 and temperature of 95±2 °C was performed. The process of hydrolysis was carried out in the heat-resistant conic flasks installed on the asbestos grids and connected with reverse refrigerators. After completion of hydrolysis, MCC was rinsed with distilled water to a neutral reaction, dried in the open air and the quality indexes of the pulp were identified according to standard methods [16].

Analysis of the change of structural characteristics of hemp MCC, depending on the stage of their treatment in the process of MCC obtaining, was investigated using scanning electronic microscopy on REM-106 (SELMI, Ukraine) and X-ray structural analysis on the diffractometer Ultima IV (Rigaku, Japan).

The degree of crystallinity (DC) of samples was defined by the formula [17]:

$$CK = \frac{I_{200} - I_{am}}{I_{200}} \cdot 100, \quad (1)$$

where I_{200} is the reflex intensity (200) around 23 degrees; I_{am} is the scattered intensity of amorphous phase around 18,5 degrees.

The resistance of obtained MCC to thermal destruction, compared with hemp cellulose, was studied by the thermogravimetric analysis on the thermoanalyser Netzsch STA-409.

5. Physical and chemical studies of the changes in structural characteristics of hemp pulp

The results of the extraction of hemp fibers by solutions of KOH of different concentrations to reduce the content of mineral substances are presented in Fig. 1.

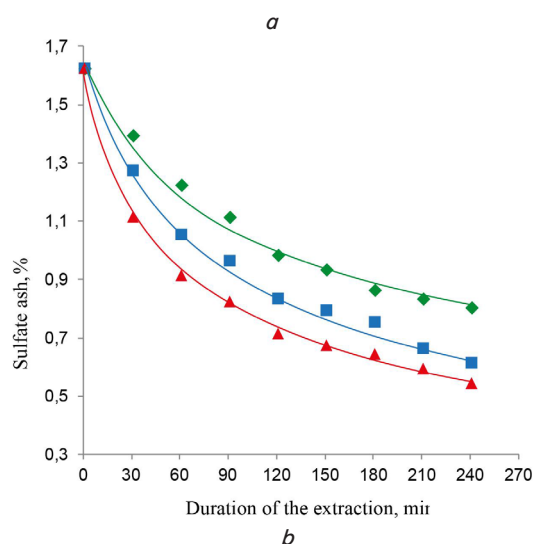
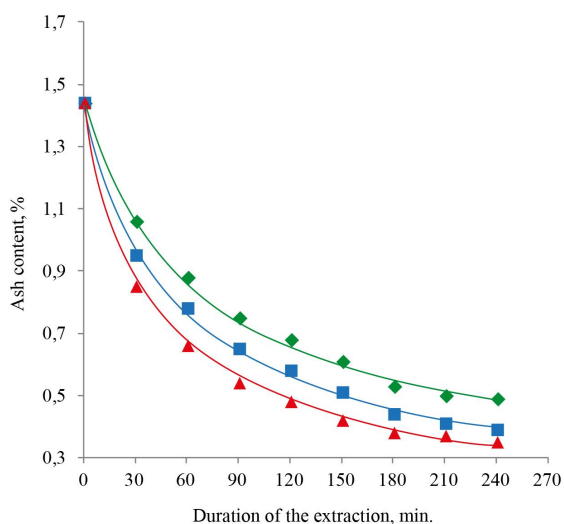


Fig. 1. Dependence of quality indexes of the hemp pulp on the concentration of KOH: *a* – ash content, %; *b* – sulfate ash, %; ♦ – KOH of concentration 3%; ■ – KOH of concentration 5 %; ▲ – KOH of concentration 7 %

As it is seen from the data shown in Fig. 1, the reduction of ash and sulfated ash in hemp pulp occurs with the increase

of duration of the extraction compared to the original plant raw material. It can be explained by the fact that during this stage, mineral substances contained in the fiber are transferred to the solution. Besides, there is a partial removal of hemicelluloses as a result of hydrolysis of low molecular weight fractions of the cellulose. Therefore, to carried out the next stages of treatment, hemp pulp was used after treatment it with a solution of KOH of concentration 5 % during 210 min.

In order to reduce the content of lignin and mineral substances on the second stage, the process of cooking cellulose by the solution of performic acid was carried out (Table 1). As it is seen from the data in Table 1, the increase the cooking duration by the solution of performic acid reduces the content of ash and sulfate ash in the hemp cellulose. Reducing the of yield of hemp pulp is caused by the destruction of carbohydrate part and by the transition of lignin, extractive substances, ash and low molecular carbohydrate compounds to the solution. There is also a sharp change of the coloring of hemp fiber from brown to white.

Table 1

Indexes of hemp cellulose after cooking in performic acid

Ratio HCOOH:H ₂ O ₂ , % volume	Duration of cooking, min	Yield of pulp, % of a.d.m.	Ash content, % of a.d.m.	Sulfate ash, % of a.d.m.
50:50	60	80,98	0,44	0,50
	90	75,83	0,35	0,37
	150	73,33	0,31	0,34
	180	72,10	0,25	0,29
40:60	150	73,85	0,29	0,35
	210	71,25	0,24	0,29
60:40	150	72,73	0,28	0,33
	210	70,10	0,21	0,25

This is due to the fact that performic acid not only destroys a lignin molecule, acting on the aromatic rings of its molecules, but causes destruction of hromofornic groups. In this case, as it is seen by the values of cellulose yield, the destructive effect of performic acid to the carbohydrate part is insignificant, because the ions of hydronium H₃O⁺, which are formed in the solution, practically do not interact with hydroxyl groups of polysaccharides.

As it is seen from the data in Table 1, minimal residual content of mineral substances in the hemp cellulose is obtained under conditions of cooking by the solution of formic acid and hydrogen peroxide in the ratio of 60:40 during 210 minutes. The considered organosolv cooking is environmentally more friendly in comparison to traditional sulphate or sulphite methods of obtaining cellulose, because harmful emissions of sulfuric and chlorine-containing compounds are absent [18, 19].

The cellulose, obtained under such conditions, was used on the next stage – chelation treatment with trilon B solution. Due to the formation of complexes of trilon B [20] with most of the cations of metals that are included into organic solvent cellulose, the residual content of mineral substances is reduced, which is important for further use of MCC in the pharmaceutical industry. Chelation treatment of organosolv hemp cellulose allows obtaining cellulose with the ash content of 0.15 % and the content of sulfated ash of 0.21 % that indicates the need to further reduce the content of mineral substances in cellulose.

In order to reduce the residual content of mineral substances and the degree of polymerization of hemp MCC, the hydrolysis of cellulose was carried out with the solution of CH_3COOH and H_2O_2 , the results of which are included in Table 2.

Table 2

Indexes of hemp MCC after hydrolysis

No. of sample	Ratio $\text{CH}_3\text{COOH}:\text{H}_2\text{O}_2$, % volume	Hydrolysis duration, min	Ash content, %	Sulfate ash, %	Degree of polymerization
1	50:50	120	0,13	0,19	210
2		150	0,09	0,15	180
3		180	0,07	0,12	150
4		210	0,07	0,12	115
5	70:30	120	0,12	0,17	160
6		150	0,08	0,13	130
7		180	0,06	0,11	100
8		210	0,05	0,10	80

According to the results of the hydrolysis (Table 2), we see that the processing of the fibers with a solution of CH_3COOH and H_2O_2 causes further reduction of ash content and sulfated ash, as well as the degree of polymerization and yield of the hemp MCC. As it is seen from the data in Table 2, a consistent implementation of various stages of the hemp fiber treatment allows obtaining hemp MCC (sample 8), which complies with the European standard by its physical appearance, pH of aqueous extracts, the degree of polymerization and the ash content [16].

6. Physical and chemical analysis of structural changes of the hemp pulp

The change of structural characteristics of the hemp pulp depending on their stage of treatment in the process of obtaining MCC could be followed on the photo of the samples received by scanning microscopy (Fig. 2). As it is seen from Fig. 2, a significant reduction of the length of hemp fibers is observed in the process of converting cellulosic fibers, especially as a result of the process of hydrolysis. MCC fibers, obtained by the proposed technology, have the length within 30...100 microns.

Confirmation of changes of the crystal structure that occur at various stages of processing hemp fibres is obtained by the X-ray structural analysis of diffractogram of natural hemp fibers, pulp after alkaline extraction, cooking and hydrolysis shown in Fig. 3.

As it is seen from Fig. 3, a consistent chemical treatment of hemp fibers by the proposed technology leads to the increase of crystallinity, the increase in the intensity of the peak about 23 degrees. Calculated values of the degree of crystallinity of the studied samples had the following values: 77.1 % – in the fibers of hemp, 84.8 % – in MCC after alkaline extraction, 87.7 % – in cellulose after cooking and 88.7 % – in MCC after hydrolysis.

The obtained data confirm the fact that the increase of content of crystalline part of cellulose occurs during a consistent multistage chemical treatment by removal of extractive and mineral substances, hemicelluloses and amorphous part of cellulose from the plant raw materials. This

fact is also confirmed by the data of the thermogravimetric analysis of cellulose and microcrystalline cellulose (Fig. 4).

As it is seen from the thermal gravimetric curves shown in Fig. 4, microcrystalline cellulose loses weight by 5–25 % less than the hemp cellulose after cooking and chelation in the temperature range between 200–300 °C. This indicates that the CMC has higher thermal stability in comparison with the hemp cellulose after cooking and chelation, which is subjected to heat destruction much faster due to the presence of less resistant to the temperature amorphous part.

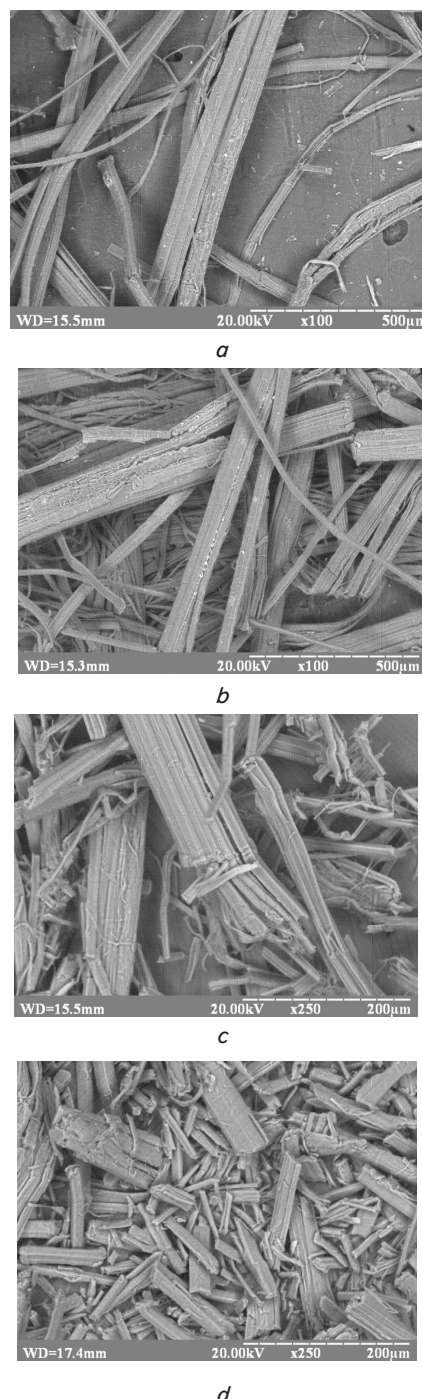


Fig. 2. Photos of SEM samples: *a* – original hemp fibers; *b* – fibers after the extraction with a solution of KOH; *c* – cellulose after cooking by performic acid; *d* – MCC after hydrolysis

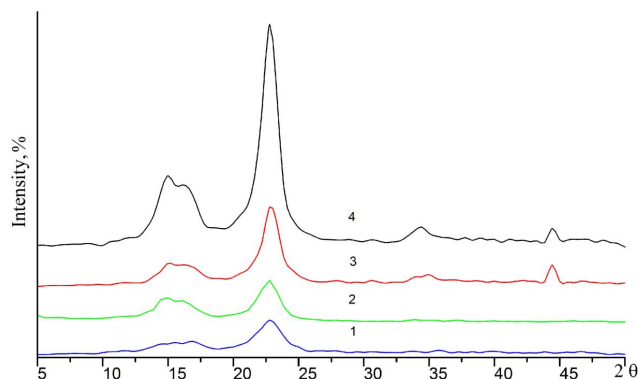


Fig. 3. X-ray structural diffractograms of hemp fibers samples (1), pulp after alkaline extraction (2), after cooking (3) and MCC after hydrolysis (4)

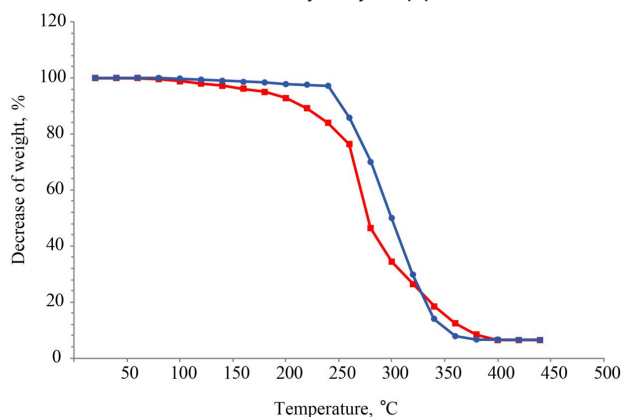


Fig. 4. Results of thermal gravimetric analysis of the hemp cellulose after cooking and chelation (■) and MCC after hydrolysis (●)

7. Conclusions

1. The influence of the main technological parameters of various stages of treatment hemp fibres on the indicators of the quality of the obtained pulps was studied. It was found that increasing the concentration of the solution of potassium hydroxide and the duration of the stage of alkaline extraction significantly reduces the content of mineral substances in the fibres of hemp. It was shown that the increase in the content of formic acid in the composition of cooking solution contributes to further reduction of mineral substances in cellulose as well as performing the stage of chelation with the solution of trilon B. It was determined that the increase of acetic acid in the mixture on the stage of hydrolysis allows obtaining MCC from hemp fibres, which meets the requirements of international standards. The proposed technology of obtaining microcrystalline cellulose from hemp fibres using organic substances does not contain harmful sulfuric and chlorine-containing compounds and therefore is environmentally more friendly.

2. The changes of structural characteristics of pulp from hemp fibres with the use of scanning electronic microscopy, thermographic and X-ray structural analyses were explored.

3. It was found that in the process of consistent treatment of hemp fibres by the proposed stages: alkaline extraction – performic cooking – chelation – hydrolysis, the reduction of length of the fibres of cellulose to microsized (up to 30–100 microns) occurs as well as the gradual removal of amorphous fraction of cellulose, which increases the degree of crystallinity from 77.1 % to 88.7 % and increases the thermal stability of the obtained microcrystalline cellulose by 5–25 %.

References

1. Audu-Peter, J. D. Physicochemical and Powder Properties of alpha- and microcrystalline-cellulose derived from sugar cane cobs [Text] / Audu-Peter, J. D., Ojile, J. E., Bhatia, P. G. // *Journal of Pharmacy & Bioresources*. – 2004. – Vol. 1, Issue 1. – P. 41–45. doi: 10.4314/jpb.v1i1.32047
2. El-Sakhawy, M. Physical and mechanical properties of microcrystalline cellulose prepared from agricultural residues [Text] / M. El-Sakhawy, M. L. Hassan // *Carbohydrate polymers*. – 2007. – Vol. 67, Issue 1. – P. 1–10. doi: 10.1016/j.carbpol.2006.04.009
3. Cintil, J. Ch. Review of recent research in nanocellulose preparation from different lignocellulosic fibers [Text] / J. Ch. Cintil, M. Lovely, Th. Sabu // *Rev. Adv. Mater. Sci.* – 2014. – Vol. 37. – P. 20–28.
4. Shlieout, G. Powder and mechanical properties of microcrystalline cellulose with different degrees of polymerization [Text] / G. Shlieout, K. Arnold, G. Muller // *AAPS PharmSciTech*. – 2002. – Vol. 3, Issue 2. – P. 45–54. doi: 10.1208/pt030211
5. Barbash, V. A. Mikrokristalichna celyuloza iz lubyanih roslin [Text] / V. A. Barbash // *Naukovi visti NTUU “KPI”*. – 2013. – Vol. 1. – P. 117–122.
6. Krotov, V. S. Novaya tehnologiya proizvodstva celyulozy sohranit les i prirodu [Text] / V. S. Krotov, A. Ya. Frank, G. A. Ryzhik // *Himichna promislovist Ukraini*. – 1995. – Vol. 1. – P. 2–5.
7. Stupinska, H. An environment-friendly method to prepare microcrystalline cellulose [Text] / H. Stupinska, E. Iller, Z. Zimek // *Fibres and textiles in Eastern January*. – 2007. – Vol. 15. – P. 167–172.
8. Autlov, S. A. Microcrystalline cellulose. structure, properties and applications (review) [Text] / S. A. Autlov, N. G. Bazarnova, E. J. Kushnir // *Himija rastitel'nogo syr'ja*. – 2013. – Vol. 3. – P. 33–41.
9. Ciolacu, D. Amorphous cellulose – structure and characterization [Text] / D. Ciolacu, F. Ciolacu, V. I. Popa // *Cellulose Chem. Technol.* – 2011. – Vol. 45, Issue 1-2. – P. 13–21.
10. Vanhatalo, K. Effect of mild acid hydrolysis parameters on properties of microcrystalline cellulose [Text] / K. Vanhatalo, O. P. Dahl // *BioResources*. – 2014. – Vol. 9, Issue 3. – P. 4729–4740. doi: 10.15376/biores.9.3.4729-4740
11. RU Patent 2203995. Method for the microcrystalline cellulose producing [Text] / Danilov V. G., Yatsenko O. V., Kuznetsova S. A., Kuznetsov B. N. – Institut himii i himicheskoy tehnologii SO RAN. – Declared: 09. 07.2002.

12. Vurasko, A. V. Appropriate technology of cellulose materials obtaining during agricultural wastes utilization [Text] / A. V. Vurasko, B. N. Driker, E. A. Kozyrev // Chemistry of plant raw material. – 2006. – Vol. 4. – P. 5–10.
13. Barbash, V. A. Vplyv stadii obrobky volokon lubyanih kultur na pokaznyky mikrokrystalichnoi tselyulozy [Text] / V. A. Barbash, Yu. M. Nagorna // Naukovi visti NTUU «KPI». – 2014. – Vol. 2. – P. 117–120.
14. Barbash, V. A. Influence of pre-treatment of flax fibers on cellulose properties [Text] / V. A. Barbash, Yu. A. Nahorna // Eastern-European Journal of Enterprise Technologies. – 2014. – Vol. 4, Issue 6 (70). – P. 4–8. doi: 10.15587/1729-4061.2014.25934
15. Barbash, V. A. Development of technology of obtaining microcrystalline cellulose from flax fibres [Text] / V. A. Barbash // Eastern-European Journal of Enterprise Technologies. – 2015. – Vol. 1, Issue 5 (73). – P. 42–46. doi: 10.15587/1729-4061.2015.36013
16. European Pharmacopoeia, 7th ed. [Text]. – Council of Europe, Strasbourg, 2010. – P. 1634–1637.
17. Costa, L. A. Extraction and characterization of cellulose nanocrystals from corn stover [Text] / L. A. Costa, A. F. Fonseca, F. V. Pereira, J. I. Druzian // Cellulose Chemistry And Technology. – 2015. – Vol. 49. – P. 127–133.
18. Ferraz, A. Formic acid/acetone-organosolv pulping of white-rotted *Pinus radiata* softwood [Text] / A. Ferraz, J. Rodriguez, J. Freer, J. Baeza // Journal of Chemical Technology & Biotechnology. – 2000. – Vol. 75, Issue 12. – P. 1190–1196. doi: 10.1002/1097-4660(200012)75:12<1190::aid-jctb342>3.3.co;2-b
19. Saberikhah, E. Organosolv pulping of wheat straw by glycerol [Text] / E. Saberikhah, J. M. Rovshandeh, P. Rezayati-Charani // Cellulose Chemistry and Technology. – 2011. – Vol. 45, Issue 1-2. – P. 67–75.
20. Zharovskiy, F. H. Analytycheskaia Khymyia [Text] / F. H. Zharovskiy. – Kyiv: Vyscha shkola, 1982. – P. 472–474.