THE EVOLUTION OF THE MICROSTRUCTURE OF CANE CELLULOSE MICROFIBRILS DURING COLD CAUSTIC EXTRACTION

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Abstract: *The cellulose yield depending on NaOH concentration, as well as time of cold caustic extraction (CCE) of cane has been investigated. Modeling of the extraction process has been carried out by the method of bivariate interpolation of the received dependence. Optimal NaOH solution concentration (12-13%) and time of extraction (3.5-4 days) have been defined. Behavior of cellulose fibers allocation in transversal dimension, depending on the CCE process conditions has been determined. At the parameters near to optimal, microfibrillar fibers with the average transverse dimension ~11 μm have been received. The decrease of this index to 9 μm may be due to an increase in the concentration of NaOH to 18 mass %. Increase of the process duration from 4 to 7 days does not affect the average transverse dimension of the fibers, but increases the homogeneity of their distribution at this indicator.*

Keywords: *cellulose, cane, microfibrils, extraction, morphology, modeling, image analysis.*

1 INTRODUCTION

The use of renewable natural resources is one of the strategic directions of the development of modern technologies, which is connected with the environmental problems of the present, as well as with the necessity to create environmentally safe materials [1-3]. The most commonly used eco-friendly filler for synthetic polymers is cellulose, which is traditionally derived from wood of different breeds. Nowadays, other "non-wood" sources of fiber cellulose semi-finished products, including kenaf, jute, ramie, straw of cereal crops, etc., are intensively investigated [4].

One of the popular areas of these studies is the use of bamboo (*Bambúsa*) as a rapidly recovering resource of fibrillar cellulose with high stress-strain properties [5-8]. The cane (*Phragmites australis*), like bamboo, belongs to the grass family (*Gramíneae*). This cosmopolitan plant is widespread throughout Europe, forming large array of thickets in the deltas and floodplains of rivers, on the banks of lakes and swamps. The biological feature of the cane is a perennial root system, from which annual annulus grow up to 5-6 m in height [9]. Stems that die in autumn accumulate in aquatic ecosystems, which eventually lead to a deterioration of the ecological situation of reservoirs. Harvesting the cane in winter can be an important component of the rational use of ecosystem resources and an important regulatory mechanism [10].

The above stipulates the feasibility of conducting research in the use of cane as a raw material for the production of environmentally safe microfibrillary cellulosic fillers of various applications, in particular for the production of polymer biocomposite materials.

There are a few chemical methods of cellulose selection which are based on the treatment by different reagents. A method of "cold" delignification is traditional and widely used for the selection of bast fibres from plant row material such as flax, hemp, linen, etc. [11]. Its essence lies in the presoaking of raw materials in water (as a rule, for a few weeks) at an ordinary temperature, which results in destruction of microfibrillar connections under the effect of physical and biological factors. It is possible to force the cold delignification process using caustic water solutions. This method is known as "cold caustic extraction" (CCE), and due to its environmental friendliness and energy efficiency attracted attention of the researchers [12-14].

The aim of the research was the study of influence of "cold caustic extraction" parameters process on the structure and dimension properties of microfibrillar cellulose fibres from cane.

2 MATERIALS AND METHODS

The main research object is a cellulose-based plant – cane (phragmites australis). There was used the middle part of the dry stem collected in the winter after the end of the growing season.

After longitudinal crushing (~30x2 mm), the weight (~1-2 g) of the plant stem was dried to constant mass. After that, 100 gr. weight was filled with aqueous solution of NaOH (20°C) at a given concentration. The extraction time lasted for 1-7 days. The concentration of aqueous solutions of NaOH was in the range of 2-18%. After the extraction process was completed, the obtained fibers were washed with a weak (1%) solution of H_2SO_4, then with distilled water to neutralize and dried to permanent weight.

The morphology of the samples was studied by optical polarization microscopy (Biolam S-11). Registration of digital images was carried out using a special eyepiece nozzle. To determine the dimensional characteristics of the fibers, a method for analyzing digital images was used, followed by a statistical processing of the data obtained.

To simulate the extraction process, the method of bivariate interpolation of Akima IMSL was used to calculate the values of the interpolation function at the points of the regular network by the values of irregularly distributed data points [15].

3 RESULTS AND DISCUSSION

The main technological parameters influencing the CCE process are the caustic concentration as well as the extraction time. The influence of these parameters on cellulose output, structure and dimensional characteristics of fibers were investigated.

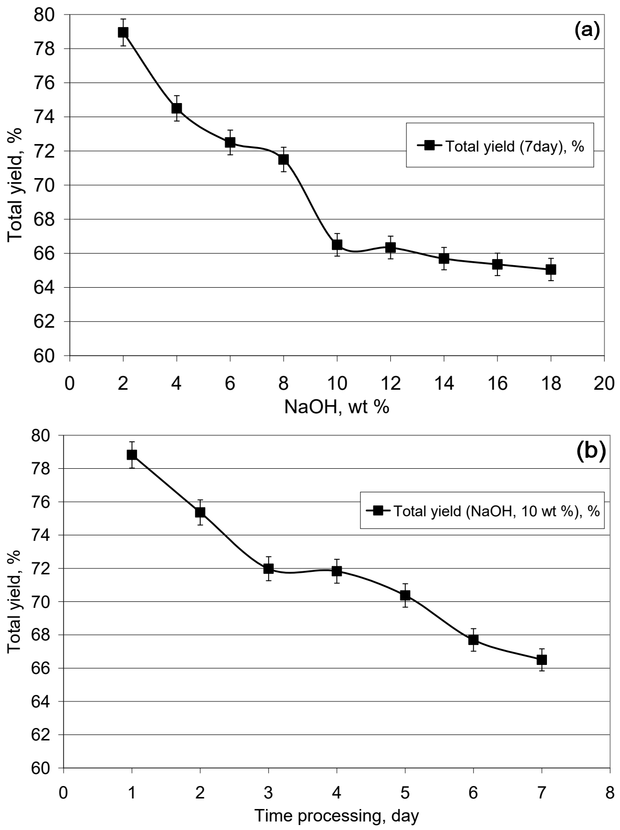

Figure 1 Dependence of the yield of cellulose on the concentration of NaOH (20°C, 7 days) (a), and time of processing (20°C, 10% NaOH) (b)

On the 2nd day of the CCE process one could observe a change in the color of the working solution from the transparent to the light brown, indicating that the extraction process proceeded. The results of the study of the caustic concentration influence in the working solution (from 2 to 18%) at a fixed time of the process (7 days) on the yield of cellulose are presented in Figure 1a.

It should be noted that the lower value of cellulose output indicates a greater completeness of the delignification process. From Figure 1, it can be seen that an increase in the concentration of caustic from 2 to 10% leads to a virtually linear decrease in the yield of cellulose from 79 to 66.5%. With a further increase in concentration from 10 to 18%, the change in the yield of cellulose is not significant. Thus, the rational concentration of NaOH solution, at given conditions of the CCE process, corresponds to the interval of 10-12%.

The study results of the influence on the effect of the cane extraction time on cellulose output at a fixed (10%) concentration of NaOH solution are shown in Figure 1b. The data shows that an increase in the extraction time from 1 to 7 days leads to almost linear decrease in the yield of cellulose from 78.8 to 66.5%. It is interesting to note that on the 3-4th day of the research, the cane yield is practically the same. This may be due to the complicated step-by-step process of simultaneous extraction of several substances from natural raw materials.

The experimental dependences of the cellulose yield on the concentration of NaOH and the time of the process allow us to construct a general approximation model that binds these indices.

The result of interpolation modeling of cellulose yield from caustic concentration and extraction time is shown in Figure 2.

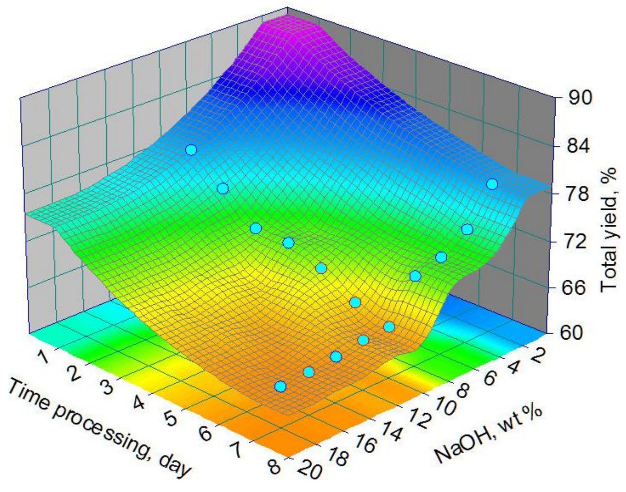

Figure 2 The 3D surface diagram obtained by the method of interpolation simulation of the dependence of cellulose yield on concentration and time of processing. The points are marked with experimental data

The approximation of the experimental data by the surface and the subsequent design of the surface to the plane allows to obtain a map of the lines which is presented for the investigated systems in Figure 3.

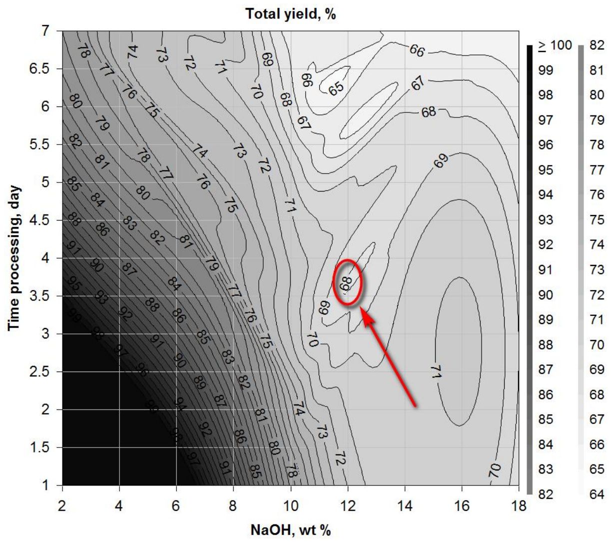

Figure 3 Map of the line levels of the interpolation model for cellulose yield from caustic concentration and time of processing

This map shows that the effect on the yield of cellulose concentration of NaOH in the working solution is more significant than the effect of the extraction process time. The optimization of process parameters is possible based on the need to achieve a satisfactory yield of cellulose at the lowest values of the concentration of caustic and the duration of the process. The given simulation results allow to predict that the optimal values (indicated by the ellipse in Figure 3) of NaOH concentration and process duration, which provide satisfactory (68-69%) yield of cellulose, make up 12-13% and 3.5-4 days respectively. The experimental testing of cellulose yield at the specified parameters of the delignification process showed that the obtained value (67.8%) is well consistent with the model representations.

The image analysis method defines the average transverse dimensions and the distribution of this index of fibers (Figure 4).

The results of the studies indicate that an increase in the concentration of NaOH in the working solution from 2 to 10% causes a decrease in the following distribution parameters (shown in the histogram heading):

- average transverse dimension of fibers (from 14.2 to 11.4 μm);
- an interval corresponding to the largest fraction of fibers (from 10-12 to 8-10 μm);
- standard deviation (from 6.5 to 4.4 μm);
- scale of distribution (from 3-50 to 3-34 μm).

According to the calculations, the coefficients of variation (~7%) and oscillations (~59%) of the aggregate also decrease. Thus, as a result of an increase in the concentration of NaOH in the working solution from 2 to 10%, the displacement of the distribution of the transverse dimension of fibers towards the lower values and their narrowing occurs.

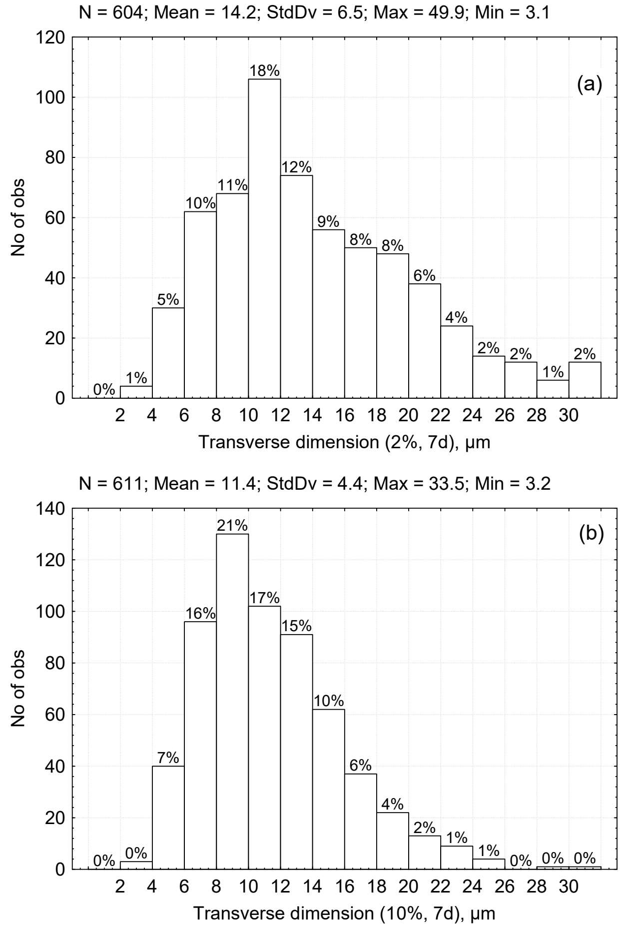

Figure 4 Histogram of transverse size distribution of cellulose microfibrils, isolated from cane by treatment with NaOH (a) 2 wt.%; (b) 10 wt.% (20°C, 7 days)

At the highest (from the investigated) concentration of caustic in the working solution (18%), the mean value of the transverse dimension of the fibers is reduced to 9.3 μm, while maintaining the values of the standard deviation of the distribution (Figure 5).

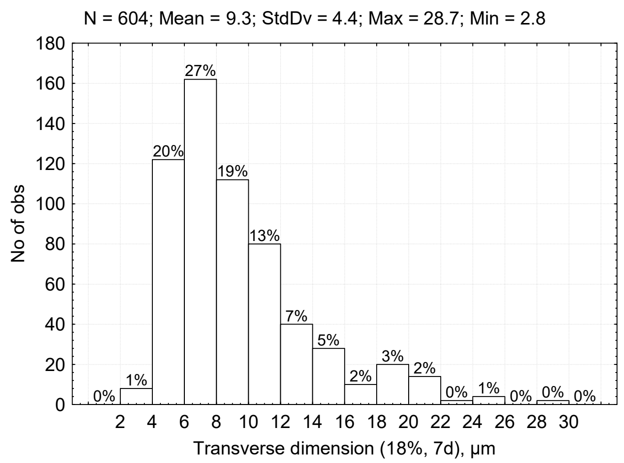

Figure 5 Histogram of transverse size distribution of cellulose microfibrils, isolated from cane by treatment with NaOH (18 wt.%; 20°C, 7 days)

Compared with the previous case (Figure 4b), the largest proportion of fibers increases from 21 to 27% and the interval corresponding to it decreases to 6-8 μm.

It should be noted that with increasing caustic concentration in the working solution from 10 to 18 wt.%, the yield of cellulose decreases slightly (~2%), while the decrease in the average transverse dimension of fibers is quite significant (by 18%). Extremely (~3 times) increases the proportion of fibers with transverse dimensions >6 μm. These results may indicate that at 10% caustic concentration, the equilibrium completeness of the delignification process of the raw material is achieved. At the same time, increasing the concentration of NaOH in the working solution to 18%, stimulates further defibrillation of fibers and reduce their transverse dimensions.

Figure 6 shows microphotographs of cellulose microfibrils obtained by cold caustic extraction in 10 wt.% of NaOH solution at different times of this process.

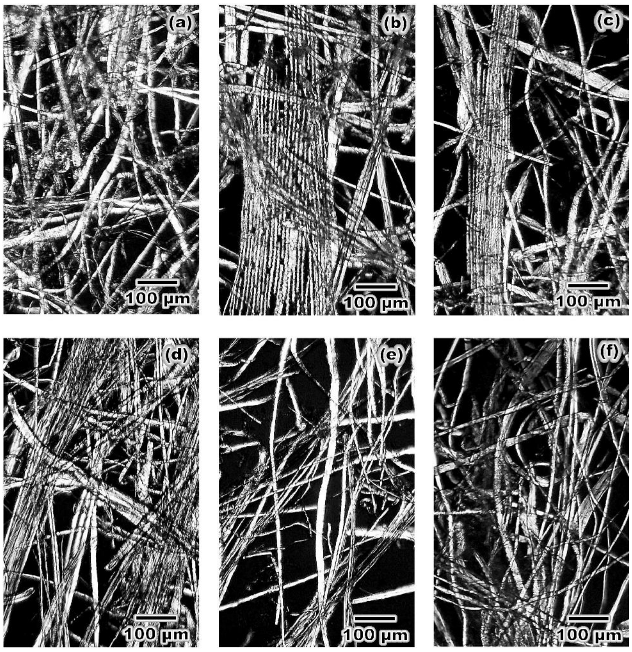

Figure 6 PLM image with crossed polars of cane cellulose microfibrils, extracted from cane by treatment with NaOH (20°C, 10 wt.%). Time of processing (a) 1 day; (b) 2 days; (c) 3 days; (d) 4 days; (e) 5 days; (f) 6 days

One can see that increasing of extraction time leads to a change in dimensional characteristics of cellulose fibers and their uniform distribution according to this indicator. This is especially noticeable for samples with extraction time >4 days (Figure 6e-f).

Figure 7 shows distribution histograms for the transverse dimension of cellulose microfibrils obtained by extraction in 10 wt.% of NaOH solution at different time of the process. They show that after the first day of the extraction process (a) the largest proportion of fibers (27%) has a dimension of 10-12 μm. The proportion of fibers with a transverse dimension <10 μm and >12 μm is respectively 32 and 40%. It should be noted, however, that in the latter case, the fiber share >12 μm refers to a much wider range of dimension (12-30 μm) than for fibers with a transverse dimension <10 μm (2-10 μm). A substantial proportion of fibers larger than the average may indicate incompleteness of the delignification of the raw material at such a time of the CCE process.

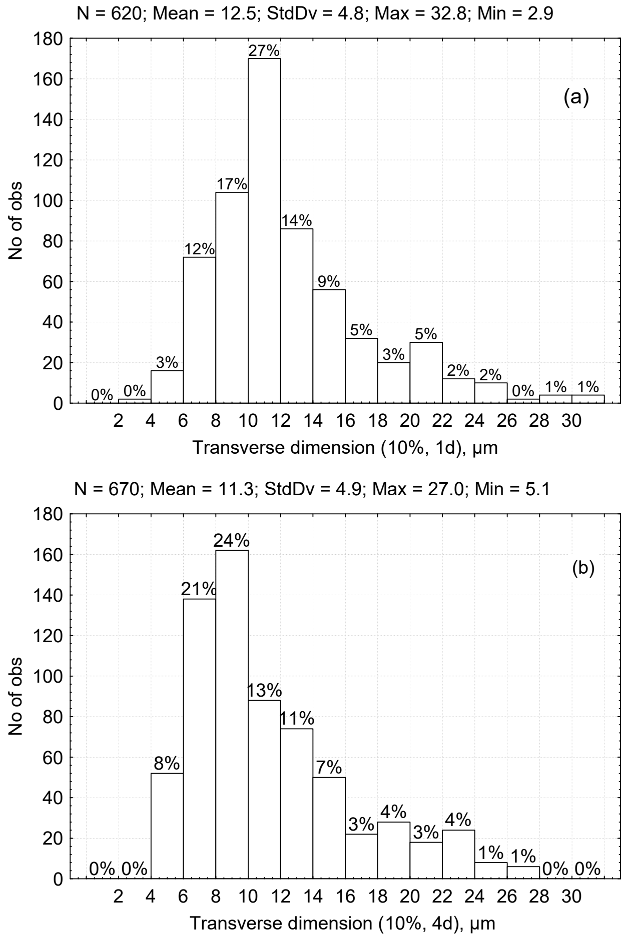

Figure 7 Histogram of transverse size distribution of cellulose microfibrils, isolated from cane by treatment with NaOH (20°C, 10 wt.%). Time of processing (a) 1 day; (b) 4 days

Increasing the extraction time up to 4 days (which approximates the optimal parameters of the model) leads to a decrease in the average transverse dimension of the fibers from 12.5 to 11.3 μm while maintaining the values of the standard deviation of the distribution (Figure 7b). At the same time, the interval corresponding to the largest (24%) fraction of fibers decreases to 8-10 μm. The transverse dimension of more than half of all fibers (53%) does not exceed 10 μm. The proportion of fibers with a transverse dimension >12 μm decreases to 34%. Thus, as a result of an increase in the time of the process, the bias of the distribution towards the lower values occurs, which leads to a decrease in the average value of the transverse dimension of the fibers by ~10%.

The comparison of the obtained distribution data shown in Figures 4b and 7b makes it possible to constant that increasing the length of the extraction process in 10% solution of NaOH from 4 to 7 days does not affect the average fiber dimension. At that time, the standard deviation of the distribution and the coefficient of variation are reduced (from 4.9 to 4.4 and 4.8% respectively), which indicates an increase in the homogeneity of the distribution at this indicator.

4 CONCLUSIONS

Dependences of the yield of cellulose on the concentration of NaOH and the time of the process of cold caustic extraction (CCE) of the cellulosic plant cane. The modeling of the extraction process has been performed by the method of bivariate interpolation of the obtained dependences. This allowed to establish the optimal concentration of NaOH solution (12-13%) and the time of processing (3.5-4 days). The experimental testing of cellulose yield at the specified parameters of the delignification process showed that the obtained value (67.8%) is well consistent with the model representations.

There has been established the nature of the change in the distribution of cellulose microfibrils in transverse dimensions, depending on the conditions of the CCE process. At parameters close to optimal, fibers have been obtained with average transverse dimensions of ~11 μm. The decrease of this index to 9 μm may be due to an increase in the concentration of NaOH to 18 wt.%. Increasing the duration of the process from 4 to 7 days does not affect the average transverse dimension of the fibers, but increases the uniformity of their distribution at this indicator.

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