The effects of hemicelluloses and lignin removal on water uptake behavior of hemp fibers

Biljana M. Pejic, Mirjana M. Kostic *, Petar D. Skundric, Jovana Z. Praskalo

Textile Engineering Department, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

Abstract

This study investigated the individual influences of hemicelluloses and lignin removal on the water uptake behavior of hemp fibers. Hemp fibers with different content of either hemicelluloses or lignin were obtained by chemical treatment with 17.5% sodium hydroxide or 0.7% sodium chlorite. Various tests (capillary rise method, moisture sorption, water retention power) were applied to evaluate the change in water uptake of modified hemp fibers. The obtained results show that when the content of either hemicelluloses or lignin is reduced progressively by chemical treatment, the capillary properties of hemp fibers are improved, i.e. capillary rise height of modified fibers is increased up to 2.7 times in relation to unmodified fibers. Furthermore, hemicelluloses removal increases the moisture sorption and decreases the water retention values of hemp fibers, while lignin removal decreases the moisture sorption and increases the water retention ability of hemp fibers.
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1. Introduction

In the situation of the intensive growth of world population and the lack of comfort and ecological fibers, solutions may be found in the return to almost forgotten natural fibers, like hemp fibers. Hemp (*Cannabis sativa*) is traditionally used for production of fibers. There is nowadays an increasing interest in total exploitation of the plant, with the intention of using seeds, fiber and shive as raw materials (Buschle Diller et al., 1999; Dang and Nguyen, 2006; Gumuskaya et al., 2007; Kozlowski et al., 2000; Wang et al., 2003).

Technical (multi-cellular) hemp fibers, obtained from hemp plant, are composed of a number of elementary fibers held together by pectinous gums, of which the main component is pectins of the middle lamellae and the primary wall. The pectins of the middle lamellae are encrusted with lignin, which makes it even more difficult to split the bundles into fibers. Lignin, providing rigidity to the cell wall, is located in the middle lamellae and secondary wall. Both pectins and lignins can be more or less strongly associated with the cellulose microfibrils. Hemicelluloses are deposited as the amorphous and unoriented cell-wall constituent, which occupy spaces between the fibrils in both primary and secondary walls. They are insoluble in hot water and primarily hydrogen-bonded to cellulose. Each elementary fiber can be considered as a network of ultrafine cellulose fibrils embedded in a matrix of hemicelluloses and lignin. In raw hemp fibers the cellulose content is about 67–78%, the rest is approximately 5.5–16.1% hemicelluloses, 3.7–8% lignin, 0.9–4.3% pectin, and some fats and waxes (Buschle Diller et al., 1999; Milosavljevic et al., 2004; Wang et al., 2003).

As a textile fiber, hemp possesses a range of extraordinary properties as: antimicrobial properties, extremely quick absorption of humidity accompanied with quick drying, good thermal and electrical properties (increased heat of sorption and low static electricity charges), outstanding

* Corresponding author. Tel.: +381 11 3303 628; fax: +381 11 3370 387.
  E-mail address: kostic@tmf.bg.ac.yu (M.M. Kostic).

tenacity (50–90 cN/tex), lack of allergenic effects, biodegradability and protection against UV radiation (Brazis et al., 2000; Czekalski et al., 2000; Kozlowski et al., 2000; Milosavljevic and Tadic, 2001; Mussig et al., 1998). However, high quantity of noncellulosic components in hemp fibers (hemicelluloses, lignin, pectin and waxes) and impurities negatively influence further fiber processing and fiber properties (fineness, elasticity, evenness, and sorption properties). The predominant task in preparing hemp fibers for further fiber processing is to remove these noncellulosic components with improving fiber properties (sorption properties, fineness, etc.) and without damage to the fiber cellulose (Buschle Diller et al., 1999; Kostic et al., 2008; Wang et al., 2003).

In this paper the influence of chemical composition (i.e. the effects of hemicelluloses and lignin removal) on the water uptake behavior of hemp fibers was studied. Hemp fibers with different content of either hemicelluloses or lignin were obtained by chemical treatment with 17.5% sodium hydroxide or 0.7% sodium chlorite. The first treatment progressively removed hemicelluloses keeping the lignin content unchanged and the last vice versa. Taking into account the fact that the direct measurement of contact angle is too complex in the case of multi-cellular hemp fiber because of its heterogeneous surface, the capillary rise method was applied to evaluate the change in wettability of hemp fibers and results obtained were treated on the basis of the general wettability relationships. The sorption properties of hemp fibers were evaluated as moisture sorption and water retention power. On the bases of the results obtained in this study, an attempt has been made to explain the individual roles of the hemicelluloses and lignin removal in the water uptake behavior of the chemically-modified hemp fibers.

2. Methods

2.1. Materials

Domestic water-retted long hemp fibers from Backi Brestovac (Serbia) were used in this investigation. The content of long fibres in the bundle was 74%, of short and tangled ones 24.2% and of shives and dust 1.8%. All used chemicals obtained from commercial sources are p.a. grade.

2.2. Chemical treatment

Hemp fibers were modified by chemical treatments in an attempt to gradually remove either hemicelluloses or lignin. The progressive removal of the hemicelluloses was brought by treating the fiber samples with 17.5% NaOH solution, 1:50 liquor ratio, at room temperature, for 5, 10, 20, 30 and 45 min, followed by neutralisation with 1% acetic acid, washing and drying. The progressive removal of lignin was achieved by treating hemp fibers with 0.7% NaClO$_2$ at pH 4, 1:50 liquor ratio, at boil temperature, for different periods of time (5, 15, 30 and 60 min), followed by washing and drying.

For removal of the hemicelluloses and keeping the lignin content unchanged and vice versa, alkali solution of 17.5% concentration and 0.7% chlorite solution were chosen from the procedure for determination of hemicelluloses and lignin content in bast fibers (Garner, 1967), only duration of treatments were shortened.

2.3. Determination of weight loss and chemical composition

Loss in weight, as result of chemical treatment, was determined by the direct gravimetric method (Koblyakov, 1989). Chemical composition of unmodified sample and each of modified samples was determined according to the scheme of Soutar and Bryden (Garner, 1967) by successively removal of water solubles, fats and waxes, pectin, lignin and hemicellulose. The results were the average of three parallel determinations.

2.4. Capillary rise measurements

Capillarity can be defined as the macroscopic movement of a fluid system under the influence of their own surface, difference in pressures and interfacial forces. Equilibrium will happen when the capillary action is balanced by gravity, that is, by the weight of the raised liquid (Wong et al., 2001). The evaluation of capillarity of fibers depends to a large extent on the measuring conditions. Also, as a natural bast fiber, hemp showed great variation in chemical composition and fiber diameter even within a single fiber. For this reason, several series of experiments have been done as a function of number of fibers (single fibres and fiber bundles) and wetting liquid (0.1% aqueous solution of eosin (viscosity 1.03×10^{-3} Pa s) and transformer oil (viscosity 28.84×10^{-3} Pa s)). The wetting liquids were chosen because of their different polarity and affinity towards hemp fibers.

Hemp fiber bundles of an approximate fineness of 500 tex were shaped in 0.5 cm width strips of maximally parallelized fibers. The length of fibers and strips was the same −30 cm.

For capillary rise measurements, the apparatus of original construction composed of 10 glass test tubes placed in a horizontal row, was used. The samples were lowered in the test tubes with metal rods. The depth of samples immersion in the liquid was 20 mm. The test tubes enabled the constant atmosphere around the sample tested. The area of the liquid surface was considerably larger than the area of the cross section of the sample, and therefore the liquid absorbtion by the sample did not change the level of the liquid significantly.

The liquid capillary rise height was easily read with the help of a ruler marked off in millimeters assembled along each sample. Height readings were made at time intervals of 10 s in the first minute, 60 s in the following 9 min and every 5 or 10 min up to attaining the equilibrium of capillary rise. The results were the average of 10 parallel read-

ings, and they were further treated on the basis of the general wettability relationships (Ferrero, 2003; Kymalainen et al., 2001; Labajos-Broncano et al., 1999; Washburn, 1921), as it is described below.

In the equilibrium, the maximum height h_{eq} of the front of capillary rise is defined by

$$h_{eq} = \frac{2 \cdot \gamma \cdot \cos \theta_{eq}}{\rho \cdot g \cdot R_S} \qquad (1)$$

where γ is the surface tension and ρ the density of the liquid, R_s the average static radius of pores, g the acceleration due to gravity (9.81 m/s^2), and θ_{eq} is the equilibrium, static contact angle, which is generally smaller than the dynamic contact angle.

At the beginning of the process, when the height reached by the liquid – h is much smaller than h_{eq}, the hydrostatic pressure can be neglected and h^2 is proportional to time

$$h^2 = D \cdot t \qquad (2)$$

where the slope D presents the coefficient of capillary diffusion, directly related to the average equivalent radius of the capillaries in porous fiber structure, chemical composition of fiber surface and physico-chemical characteristics of the liquid (Ferrero, 2003).

In the case when h is close to h_{eq} the hydrostatic pressure cannot be neglected and by introducing the approximation that $\theta = \theta_{eq}$, the following equation is obtained:

$$h_{eq} \cdot \ln \frac{h_{eq}}{(h_{eq} - h)} - h = \frac{R_D^2 \cdot \rho \cdot g}{8 \cdot \eta} \cdot t \qquad (3)$$

where R_D is the average hydrodynamic radius of pores, and η the liquid viscosity.

Eq. (3) can be presented, as Ferrero (2003) suggested, in a simplified form

$$H = C \cdot t \qquad (4)$$

Graphical presentation of the function $H = f(t)$ is the straight line with the slope C being dependent only on the size of the capillaries in fibers and to the nature of the liquid.

As the measure of validity of the assumption $\theta = \theta_{eq}$ the following ratio can be used:

$$R = \frac{\cos \theta}{\cos \theta_{eq}} = \frac{D}{2 \cdot C \cdot h_{eq}} \qquad (5)$$

This ratio is always smaller than 1, because of the fact that θ is generally larger than θ_{eq}.

By processing of obtained data, i.e. the liquid capillary rise height vs. time up to the equlibrium height is reached, through Eqs. (2), (4), and (5), and drawing corresponding curves, all three parameters of wettability (D, C and R) were determined.

2.5. Determination of moisture sorption

Moisture sorption of hemp fibers was determined according to standards (ASTM D 2654-76, 1976). Hemp fibers were exposed to standard atmosphere: $20 \pm 2\,°C$, $65 \pm 2\%$ relative humidity, for 24 h (ASTM D 1776-74, 1974). Moisture sorption was calculated as a weight percentage of absolute dry material.

2.6. Determination of water retention

Water retention of hemp fibers was determined by standard centrifuge method (ASTM D 2402-78, 1978).

3. Results and discussion

3.1. Influence of chemical treatment on chemical composition

The chemical compositions of chemically-modified hemp fiber samples, in all nine samples, and those of the control sample, and the weight loss are given in Table 1. The level of hemicelluloses removal during the alkaline treatment was high, their content dropped from 10.72% to 3.29% (about 70% removed), with slightly changed lignin content. However, a certain amount of hemicellulose residues remain in the structure because of considerably stable hemicellulose hydrogen bonding to cellulose fibrils. The sodium chlorite treatment progressively removed lignin keeping the hemicelluloses content almost unchanged, with the longest treatment about 50% of lignin was removed. A certain residual lignin level indicates that some

Table 1
The chemical compositions and weight loss of hemp and modified hemp fibers

Sample code	Modification conditions	Weight loss (%)	Hemicelluloses		Lignin	
			Content (%)	Removed (%)	Content (%)	Removed (%)
C	Unmodified sample	–	10.72	–	6.06	–
H 5	17.5% NaOH, RT, 5 min	8.15	4.69	56.25	5.66	6.60
H 10	17.5% NaOH, RT, 10 min	7.78	4.19	60.91	5.12	15.51
H 20	17.5% NaOH, RT, 20 min	9.43	4.38	59.14	5.27	13.04
H 30	17.5% NaOH, RT, 30 min	9.18	3.29	69.31	5.18	14.52
H 45	17.5% NaOH, RT, 45 min	9.90	3.59	66.51	5.41	10.73
L 5	0.7% NaClO$_2$, boiling, 5 min	4.16	8.89	17.07	4.09	32.51
L 15	0.7% NaClO$_2$, boiling, 15 min	5.47	9.78	8.77	3.74	38.28
L 30	0.7% NaClO$_2$, boiling, 30 min	5.15	8.72	18.66	3.57	41.09
L 60	0.7% NaClO$_2$, boiling, 60 min	6.17	8.99	16.14	3.09	49.01

lignin in the fibers could not be easily accessed or degraded due to the presence of strong carbon–carbon linkages and other chemical groups such as aromatic groups, which are very resistant to chemical attack. The severity of treatment is generally characterized by weight loss. Taking in consideration the chemical compositions' data together with weight loss data, it is clear that the fiber cellulose remain unimpaired.

Changes in hemp fibers composition, i.e. the separate removal of hemicelluloses and lignin, affect the water uptake behavior of these fibers, which could be expresed as capillarity, moisture sorption and water retention power. These properties are very important for both fiber processing and performance. In addition, wettability can be valuable for characterizing fiber surfaces, liquid transport, interaction of fibers with liquids and surfactants (Ferrero, 2003; Kissa, 1996; Skundric et al., 2007; Wong et al., 2001).

3.2. Influence of chemical composition of hemp fibers on their capillarity

Capillary properties of hemp fibers may have importance when selecting the use of end products. Good capillarity of fibers can be of advantage in products in which a good absorption capacity and/or speed is needed, also it allows the fiber to absorb moisture, liquids, lubricants, finishes, and stem, permitting faster bleaching, dyeing, impregnating, etc. (Kymalainen et al., 2001, 2004; Wong et al., 2001).

Measuring capillarity of single hemp fibers gives the high coefficient of variation (about 50%, see Table 2) because of the fact that hemp fiber as a natural bast fiber, showed great variation in fiber diameter even within a single fiber, and the fiber surface appeared relatively rough and uneven, with small fibrillar ends pointing away from the surface. These irregularities affect the liquid front movement, i.e. the flow in a capillary space may stop when geometric irregularities allow the meniscus to reach an edge and flatten. Keeping in mind the all above mentioned, it is reasonable to measure the capillarity of fiber bundles, which gives average values with lower coefficient of variations, Table 2.

Table 2
Capillary rise data (equilibrium height, h_{eq}; coefficient of variation, CV) for single hemp fibers and fiber bundles, as a wetting liquid 0.1% aqueous solution of eosin was used

Sample code	Single fibers		Fiber bundles	
	h_{eq} (mm)	CV (%)	h_{eq} (mm)	CV (%)
C	8.8 ± 3.3	51.6	28.4 ± 3.94	19.1
H 5	29.2 ± 12.02	56.6	49.4 ± 9.63	26.8
H 10	36.6 ± 14.08	52.9	56.4 ± 6.07	14.8
H 20	26.2 ± 10.35	54.3	42.6 ± 5.67	18.3
H 30	35.6 ± 4.22	16.3	61.4 ± 1.92	4.3

The two-sided confidence limits correspond to the significance level of 0.05.

From the data presented in Table 2 it is evident that the value of equilibrium height (h_{eq}) of capillary rise is different for single fibers and fiber bundles, but the tendency is the same. The increase of h_{eq} in the hemp fibers bundles, in relation to the single fibers, is caused by an "additional" capillary effect, which appears as a consequence of interfacial capillary forces formed between fibers within the bundle. Taking this in consideration and in order to obtain numeric values which permit good description and comparison of the capillarity of unmodified and modified hemp fibers, it is very important to prepare fiber bundles in the same manner, which will minimize influence of fibers alignment and interfiber spaces on obtained results.

The applied capillary rise method provides the collective measurements of simultaneous wetting of the fiber surface, liquid uptake in the pore structures – capillary penetration, adsorption on the fiber surface, and liquid absorption within the fibers (Wong et al., 2001). The sorption of the liquid into the fibers can cause their swelling, reduce capillary spaces into the fibers and close smaller pores, and complicate kinetics. The interpretation of results, i.e. influence of chemical composition changes on the fiber capillarity, can be misleading if the effects of sorption into the fibers are overlooked (Kissa, 1996). In our case, by the removing hemicelluloses and lignin the fiber bulk structure and moisture sorption (see Fig. 7) were changed, and we expected that both untreated and treated fibers do not have a similar swelling tendency. In order to quantify the individual contributions of wettability, sorption properties and pore structure to liquid transport and retention properties of hemp fibers we set up two series of experiments using two different wetting liquids: 0.1% aqueous solution of eosin and transformer oil. Transformer oil was selected because it has no affinity towards hemp fibers and under these measuring conditions the rise of the liquid can be attributed only to capillary effect caused by the fiber surface properties and fiber micro-porosity.

Results of capillary rise in fiber bundles of unmodified and modified hemp fibers are shown in Figs. 1–4 as h vs time. Evidently, the capillary rise is strongly enhanced by fiber modification (i.e. hemicelluloses and lignin removal) and after some time the height reaches an equilibrium value. In the case of eosin solution, the equilibrium value is attained up to 2000 s, and for transformer oil up to 120 s. The capillary rise of eosin solution for modified fibers is increased in relation to initial fibers, being 1.5–2.2 and 2.0–2.7 times higher for hydroxide and chlorite modified fibers, respectively. The oil capillary rise in modified fibers, in relation to unmodified fibers, also manifests a trend of growth, being 1.8 and 1.3–2.4 times higher for hydroxide and chlorite modified fibers, respectively. For the aqueous solution of eosin, it is obvious that we have sorption of the liquid into the fibers and fibers swelling, leading to reducing capillary spaces into the fibers and higher capillary pressure in a smaller pores, i.e. higher equilibrium capillary rise of water in comparison with transformer oil (compare Figs. 1 and 3 with Figs. 2 and 4, and the above data).
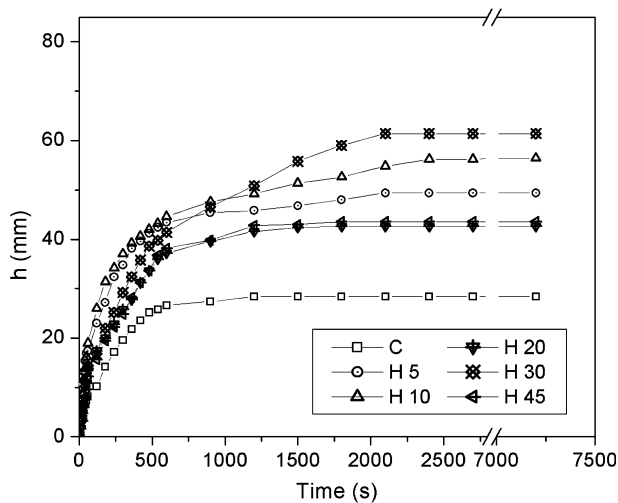
Fig. 1. Capillary rise on hemp fiber bundles modified with 17.5% NaOH for different periods of time, wetting liquid 0.1% aqueous solution of eosin.
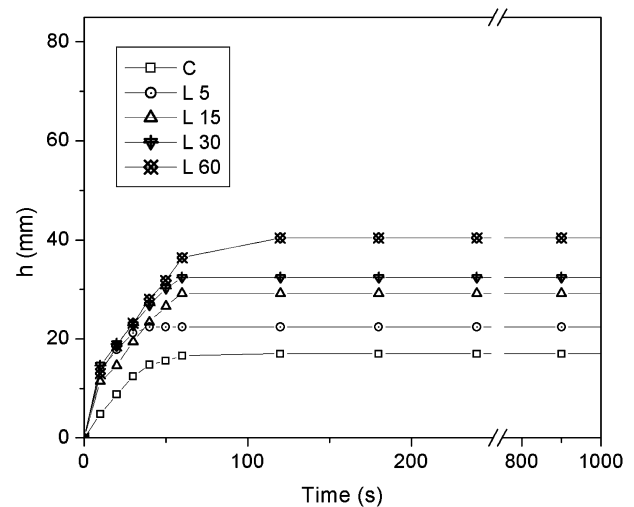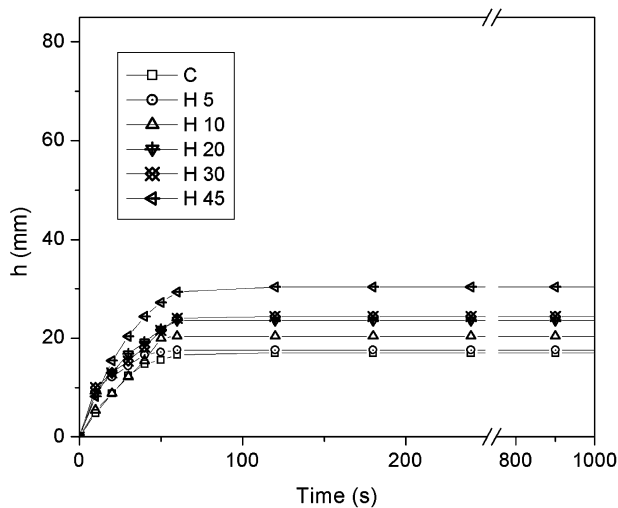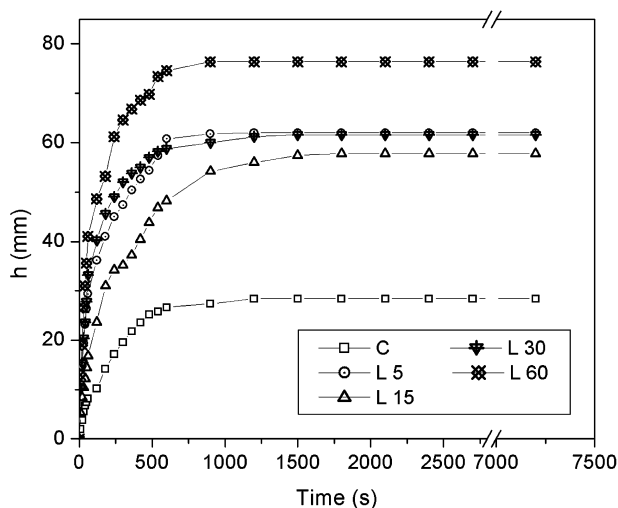

Fig. 2. Capillary rise on hemp fiber bundles modified with 17.5% NaOH for different periods of time, wetting liquid transformer oil.

Fig. 3. Capillary rise on hemp fiber bundles modified with 0.7% NaClO₂ for different periods of time, wetting liquid 0.1% aqueous solution of eosin.

Fig. 4. Capillary rise on hemp fiber bundles modified with 0.7% $NaClO_2$ for different periods of time, wetting liquid transformer oil.

The capillary principles dictate that the distance of liquid advancement is greater in a smaller pore because of the higher capillary pressure, smaller pores are filled first and are responsible for the liquid front movement, i.e. the smaller the pore radius, the equilibrium height is greater, and the more time is needed for liquid to reach the equilibrium height (Washburn, 1921). If we consider our results together with the capillary principles, it is obvious that gradual removal of lignin leads to faster liquid spreading in fibers facilitated by small, uniformly distributed and interconnected pores.

As it was explain in experimental part, the processing of obtained data, i.e. the liquid capillary rise height vs. time, through Eqs. (2), (4) and (5) and drawing corresponding curves (Figs. 5 and 6), all three parameters of wettability (D, C and R) were determined (see Table 3).

The coefficient of capillary diffusion D is clearly affected by the removing either hemicelluloses or lignin. For
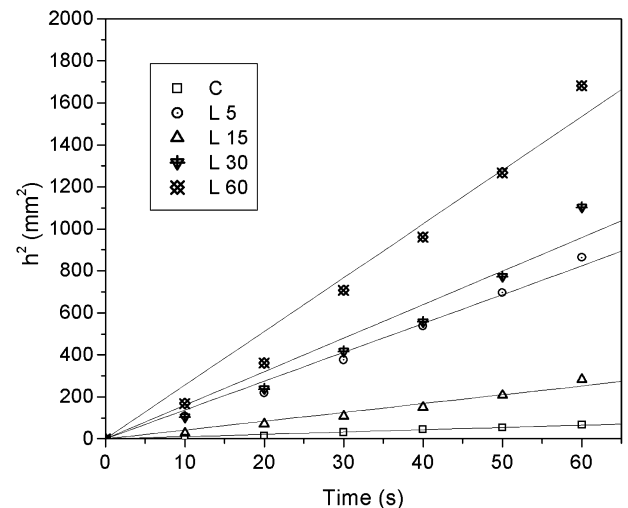

Fig. 5. The effect of lignin removal (hemp fibers modified with 0.7% $NaClO_2$) on h^2, wetting liquid 0.1% aqueous solution of eosin.
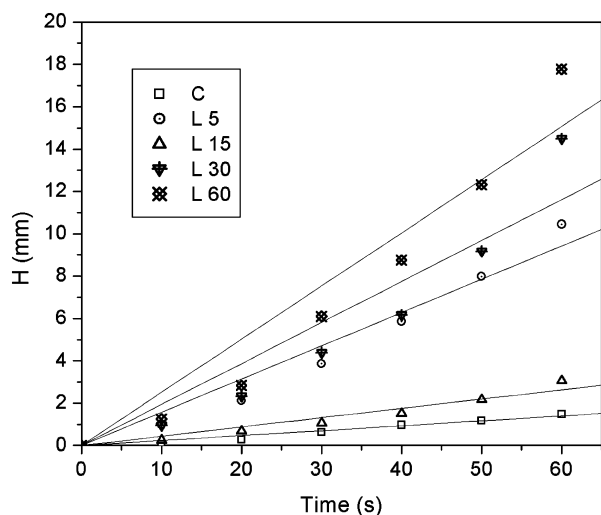
Fig. 6. The effect of lignin removal (hemp fibers modified with 0.7% $NaClO_2$) on H, wetting liquid 0.1% aqueous solution of eosin.

Table 3
Values of coefficients D, C and R for unmodified and modified hemp fibers

Wetting liquid	0.1% eozin			Oil		
Samples	D (mm²/s)	C (mm/s)	R	D (mm²/s)	C (mm/s)	R
C	1.03	0.02	0.91	4.55	0.27	0.49
H 5	5.49	0.07	0.79	7.45	0.49	0.43
H 10	5.23	0.06	0.77	4.44	0.18	0.59
H 20	2.10	0.03	0.82	9.09	0.37	0.52
H 30	3.02	0.02	1.03	8.04	0.30	0.53
H 45	1.68	0.03	0.77	12.89	0.39	0.54
L 5	13.82	0.16	0.69	15.46	1.26	0.27
L 15	4.25	0.04	0.92	12.18	0.37	0.57
L 30	16.33	0.19	0.69	17.79	0.52	0.52
L 60	25.37	0.25	0.66	17.42	0.34	0.64

modified hemp fibers, the value of coefficient D significantly increases in relation to the unmodified fibers, and this increase is more pronounced in the case of fibers with lower lignin content. The results of coefficient C, that can be made equal to the wetting rate, are spread in a range from 0.02 to 1.26 mm/s, suggesting some influence of the lignin and hemicelluloses removal on the wetting rate of modified hemp fibers. It is also obvious that the increase of coefficient C of modified hemp fibers, in relation to the unmodified fibers, is much smaller in the case of hemicelluloses removal than lignin removal. The trend of coefficients D and C of hemp fibers modified with sodium hydroxide listed in Table 3 most likely can be ascribed to the greater influence of structural changes in hemp fibers, in comparison to the changes in the hemicelluloses content. The R-values, mostly range from 0.7–1.0, confirm well enough the validity of assumption $\theta = \theta_{eq}$ in the case of wetting with eosin solution, while the values of R are lower and more scattered in the case of transformer oil.

From results obtained, it is clear that changing hemp fiber chemical compositions alter its porous structure and capillarity properties. These changes can be ascribed not only to the decrease of lignin or hemicelluloses content, but also to the influence of the location of these components in the hemp fiber structure. Treatments directed towards modification of fiber surfaces bring about changes of pore diameter and of the contact angle, both of them influencing variation of capillary rise heights and capillary diffusion coefficients.

These changes are more pronounce in the case of lignin removal and impose the conclusion that gradual removal of hemicelluloses most likely causes smaller changes of the fiber surface than gradual removal of lignin. This circumstance can be explained by the facts that removed hemicelluloses were located in the inter-fibrillar regions inside ultimate cells and that lignin which was partly removed with 0.7% $NaClO_2$ fulfilled the middle lamella joining ultimate cells. Also, reason for this probably lies in the fact that when hemp fibres are treated with 17.5% NaOH, hemicelluloses are progressively removed, making the inter-fibrillar regions less dense and rigid and thereby make the fibrils more capable to rearrangement. The removal of hemicelluloses is accompanied by swelling and shrinkage of ultimate cells, which result in some disorientation of the fibrils and texturing of hemp fibers (Buschle Diller et al., 1999; Kostic et al., 2008; Wang et al., 2003). In the case of lignin removal, occurred fibrillation induced new capillary spaces in inter-surfacial layer between completely or partially separated fibers within the technical modified hemp fiber. Due to fibrillation increased the roughness of hemp fiber surfaces can promote wetting by decreasing apparent contact angle, even the intrinsic wettability of the fibers remains the same. From the other side, when hemp fibers are treated with 0.7% $NaClO_2$ and lignin is removed gradually; the middle lamella joining the ultimate cells is expected to be more homogenous due to the gradual elimination of micro-pores, while the ultimate cells themselves are affected only slightly. According to the literature (Buschle Diller et al., 1999; Wang et al., 2003) there is no appreciable loss in molecular orientation in delignificated hemp fibers.

3.3. Effect of hemicelluloses and lignin removal on moisture sorption and water retention

Hemp fibers–water interaction can be explained as a competition of hydrogen-bond formation between hydroxyl groups of the polymer (mainly cellulose) and between that of the polymer and a water molecule or a water cluster. The water penetrates inside the fiber in the form of vapor or water in liquid state. It breaks the secondary interactions between cellulose macromolecules and is adsorbed into the fiber by hydrogen bonds, which causes a swelling of the fibers. Free hydroxyl groups at the hemp fiber amorphous regions and at the crystallites' surfaces are responsible for the moisture sorption at 65% relative humidity and 20 °C, while higher relative humidity causes physical sorption due to capillary condensation (Kreze et al., 2001; Kymalainen et al., 2004). The sorption of water

vapor starts with the formation of a monolayer, where one molecule of water is bonded to each accessible hydroxyl group and continues with the formation of a multilayer of progressively increasing thickness. Therefore, moisture sorption values yield information on the extent of areas accessible to water vapor within a fiber. Changes in moisture sorption of modified hemp fibers reflect changes in chemical composition, crystallinity, and pore structure. Moisture sorption values for unmodified and modified hemp fibers are presented in Fig. 7.

The obtained data showed that hemicelluloses removal increased the moisture sorption of hemp fibers compared to unmodified fibers; while lignin removal decreased the moisture sorption of chlorite modified hemp fibers. The highest value of moisture sorption (9.44%) was obtained for sample H 20 (sodium hydroxide modified hemp fibers during 20 min). The trend of the moisture sorption values for hemp fibers with lower hemicelluloses content presented in Fig. 7, most likely is consequence of alkali treatment under slack conditions resulting in fibers swelling, contraction of fiber lengths, and some disorientation of fibrils. The lowest value of moisture sorption (6.91%) was obtained for sample L 60 (chlorite modified hemp fibers, 60 min). The decrease of the moisture sorption with gradual lignin removal can be explained by removing the easily accessible noncellulosic moisture-absorbing materials in hemp fibers (i.e. lignin) during the chlorite treatment.

When hemp fibers are immersed in water they swell and imbibe considerably more water, than they are capable of holding. The total water holding capacity of a fiber can be estimated by determining water retention values. All water absorbing and holding surfaces, cracks, and cavities are included with the water retention measurement. The water retention power represents the quantity of water which is retained in the fibers after the prescribed soaking in the water, and centrifugation.
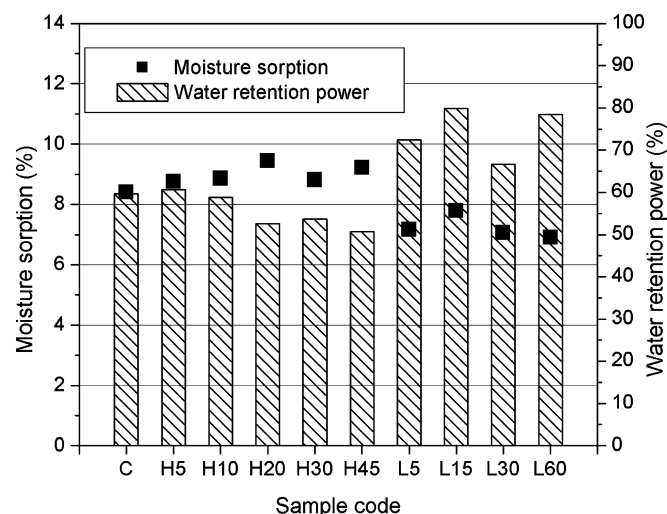
Water retention values for modified and unmodified hemp fiber are presented in Fig. 7. The results of water retention values are the opposite to that of moisture sorption, since fibers with progressively removed lignin are capable to retain more water than the unmodified and alkali treated fiber. The alkali treatment (hemicelluloses removal) yielded water retention values lower than value of unmodified hemp fibers that remained more or less constant after 20 min treatment time. The same decrease in water retention value of alkali treated fibers was also observed during alkali scouring of flax fibers by Fakin et al. (2006). The effect of lignin removal on water retention value was significant since removing about 40% of lignin results in 20% more water kept by modified hemp fibers in comparison with unmodified fibers.

The data obtained for water retention power should be always considered together with capillary rise data because water retention ability influenced liquid advancement, i.e. fibers with higher retention ability and shorter liquid advancement may have water uptake value similar to that of fibers with a longer liquid advancement and lower water retention. Therefore, fast liquid spreading in fibers is facilitated by small, uniformly distributed and interconnected pores, whereas high liquid retention can be achieved by having a large number of large pores or a high total pore volume.

4. Conclusion

This work presents an attempt to explain the individual influences of lignin and hemicelluloses on water uptake behavior of hemp fibers. The capillary diffusion coefficient D and coefficient C, related to the hydrodynamic radius of pores, are increased by removing either lignin or hemicelluloses. The progressive removal of hemicelluloses or lignin influenced the accessibility and sorption properties of hemp fibers differently, i.e. hemicelluloses removal increases the moisture sorption and decreases the water retention values of hemp fibers, while lignin removal decreases the moisture sorption and increases the water retention ability of hemp fibers. All these changes are more pronounce in the case of lignin removal and impose the conclusion that gradual removal of hemicelluloses most likely causes smaller changes of the fiber surface and accessibility than gradual removal of lignin.

Fig. 7. Moisture sorption and water retention values of unmodified and modified hemp fibers.

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