

SUPPLEMENTARY FILES FOR MANUSCRIPT:

Oxidized hemp fibers with simultaneously increased capillarity and reduced moisture sorption as suitable textile material for advanced application in sportswear

Jovana Z. Milanovic^{*,1}, Milena Milosevic², Matea Korica¹, Ivona Jankovic-Castvan³ and
Mirjana M. Kostic⁴

¹ *Innovation Center of Faculty of Technology and Metallurgy, University of Belgrade,
Karnegijeva 4, 11000 Belgrade, Serbia*

² *SI Institute of Chemistry, Technology and Metallurgy, National Institute, Department of
Ecology and Technoeconomics, University of Belgrade, Njegoševa 12, 11000 Belgrade,
Serbia*

³ *Faculty of Technology and Metallurgy, Department of Inorganic Chemical Technology,
University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia*

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

**Running head: OXIDIZED HEMP FIBERS WITH INCREASED
CAPILLARITY**

(S1) Capillary rise measurement:

Section: Material and methods

Hemp fiber bundles with the length of 20 cm were shaped in width strips of maximum parallelized fibers. One end of the strip was fixed with a clip-on the horizontal bar, and the other end was pre-loaded with 2 g tag and immersed in 0.1 % eosin aqueous solution. The depth of a sample immersion was 20 mm [1]. The liquid capillarity height was read from the recorded images. The ruler was located along the vertical plate and it allows reading in the appropriate units for the length (mm). At the same time, when the samples were immersed in eosin solution, the web camera was turned on and started to take pictures in the shorter intervals at the beginning of measurement, and we chose photos made in every 10s in the first minute, then 1 min in the next 9 min, every 5 or 10 min up to 60 min, and 20-60 min up to 240 min. The results were the average grade of three parallel readings. Capillary rise was determined on the all samples modified at RT, although in most samples oxidized on 45 °C, determination was not possible, because the fibers did not have sufficient length.

In order to determine the height of the raised liquid on the hemp fibers, digital image processing was required. Considering that rising liquid was eosin, which is orange-red color, correction of color balance was applied by using open-source software for image manipulation GIMP. The result of mentioned image processing is shown in **Figure S1** for hemp fibers oxidized with 6 % KMnO_4 , at pH 9 and room temperature, during 10 min, with maximum capillary rise height of 73 mm.

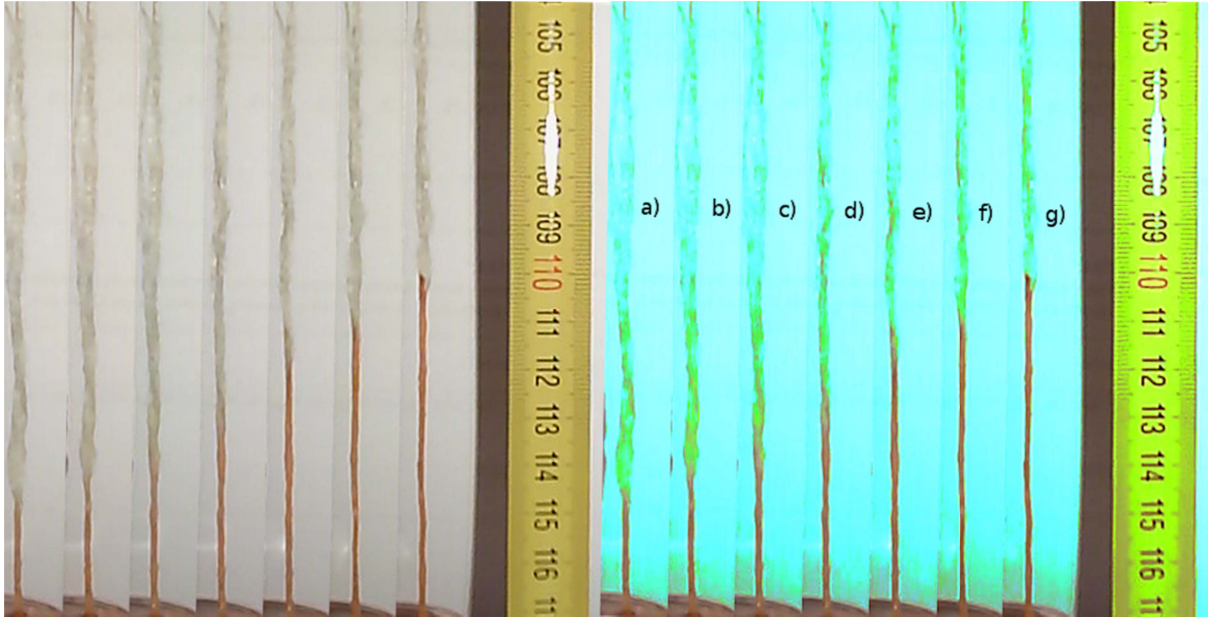


Figure S1. Determination of capillary rise of hemp fibers oxidized with 6% KMnO_4 , at pH 9 and room temperature, during 10 min, (H10): a) 1 min, 22 mm; b) 5 min, 27mm; c) 15 min, 35 mm; d) 30 min, 45 mm; e) 60 min, 54 mm; f) 120 min, 63 mm; g) 240 min, 73 mm

The liquid capillary rise height (h) was measured and presented as a function of time (t), and by processing of obtained experimental data all three wettability parameters (D , C , and R) can be calculated using equation presented in the literature [1,2], since in our measurement the equilibrium height was reached:

The maximum height h_{eq} of the front of capillary rise in the equilibrium is defined as

$$h_{\text{eq}} = (2 \cdot \gamma \cdot \cos \theta_{\text{eq}} / \rho \cdot g \cdot R_s), \quad (1)$$

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

In the case when the height reached by the liquid (h) is much smaller than h_{eq} (at the beginning of the capillary rise process), the hydrostatic pressure can be neglected and h^2 is proportional to time:

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

where the slope D presents the coefficient of capillary diffusion, that is directly related to both the size of capillaries in porous fiber structure, the contact angle between fiber surface and the liquid (Ferrero, 2003).

When h is close to h_{eq} the hydrostatic pressure cannot be neglected and with introducing the approximation where $\theta = \theta_{eq}$,

$$h_{eq} \cdot \ln [h_{eq}/(h_{eq} - h)] - h = (R_D^2 \cdot \rho \cdot g / 8 \cdot \eta) \cdot t \quad (3)$$

where R_D is the average hydrodynamic radius of pores, and η the liquid viscosity. Eq. (5) can be presented in a simplified form, i.e.

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

where parameter C presents the slope that depends only on the size of the capillaries in fibers and to the nature of the liquid.

As the measure of validity of the assumption $\theta = \theta_{eq}$, parameter R , can be determinate as:

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

(S2) The structural and chemical changes in hemp fibers caused by oxidation process

Section Results and Discussion



a) Unmodified hemp fibers (0)



b) 3 % KMnO_4 , 45 °C, pH 7, 30 min



c) 3 % KMnO_4 , 45 °C, pH 11, 30 min



e) 6 % KMnO_4 , 45 °C, pH 7, 30 min



f) 6 % KMnO_4 , 45 °C, pH 11, 30 min

Figure S2 Photos of unmodified (a) and hemp fibers oxidized under 45°C, during 30 min, with 3% KMnO_4 and b) pH 7 and c) pH 11, and with 6% KMnO_4 and e) pH 7 and f) pH 11.

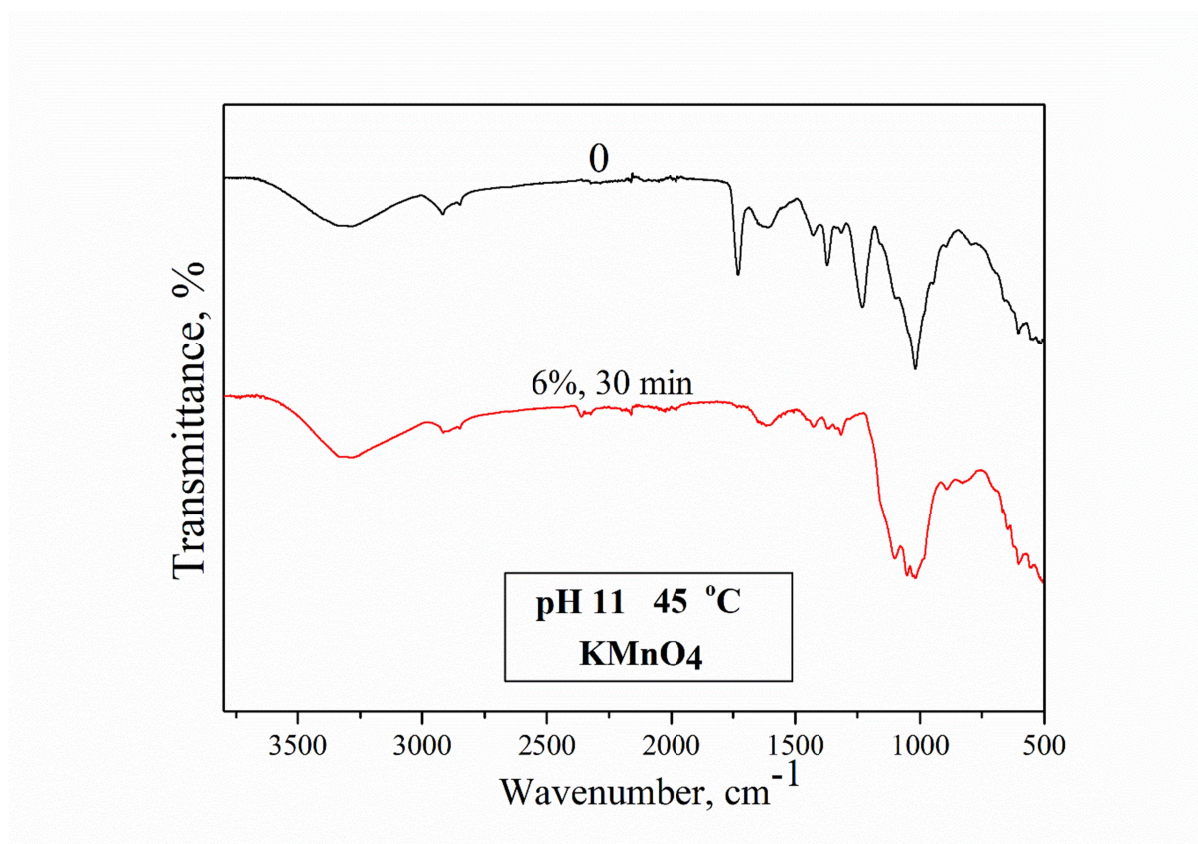


Figure S3 FTIR spectra of unmodified (0) and modified hemp fiber with 6 % KMnO_4 for 30, 30 min at 45 °C and pH 11

(S3) Deconvolution of the FTIR spectra

Section Results and Discussion

In order to get a better insight into the influence of pH and KMnO_4 concentration on the content of carboxyl and aldehyde groups present on the fiber surface, deconvolution of corresponding FTIR spectra was performed. The deconvolution was specifically applied in the region which is the most interesting to analyze degree of oxidation, *i.e.* to quantify the peaks related to ester, aldehyde, and carboxyl group, and for a period of 10 min treatments (**Figure S4**). The deconvoluted FTIR spectra of hemp fibers oxidized with 3 % KMnO_4 , under different pH values (7, 9 and 11) are shown in **Figure S4**, in order to show the influence of pH value, while for showing the influence of KMnO_4 concentration, the deconvoluted FTIR spectra of samples oxidized with 3% and 6% KMnO_4 , at pH 9, are shown.

It could be observed that absorbance of a C=O ester stretch vibration (peak in the range $1732 - 1734 \text{ cm}^{-1}$) of oxidized samples at pH 11 is significantly lower than one obtained at pH 7, which indicates greater efficiency of oxidative treatment at higher pH.

A slightly increased area of C=O group in the range $1723-1726 \text{ cm}^{-1}$ suggests the increased presence of aldehyde groups as a result of oxidation, and higher effectiveness was noticed at higher pH. Lower influence of time treatment longer than 10 min was also noticed. Also, the broad peaks in the range $1715-1700 \text{ cm}^{-1}$ indicate the presence of the significant amount of carboxyl groups on the oxidized hemp fiber. The values of peak areas from deconvoluted FTIR spectra are in good agreement with the results obtained for the aldehyde and carboxylic groups content determination.

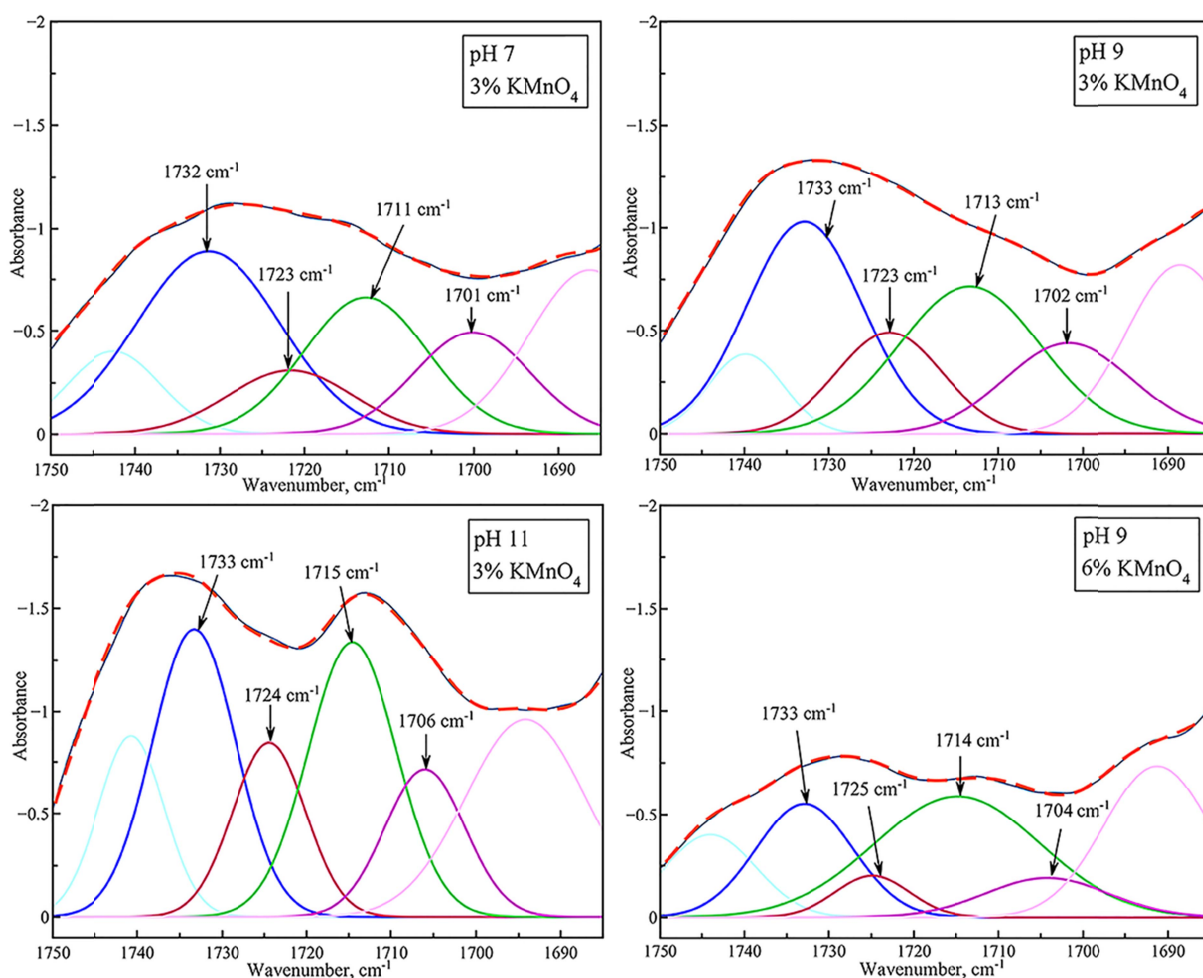


Figure S4 Deconvoluted FTIR spectra in the region $1685\text{--}1750\text{ cm}^{-1}$ related to the ester, aldehyde and carboxyl groups for hemp fibers oxidized with 3% KMnO_4 , during 10 min, at pH 7, pH 9 and pH 11, and with 6 % KMnO_4 at pH 9.

According to the obtained results, it could be observed that time-dependent oxidation processes showed high efficacy on functional groups introduction for a period of oxidation of 10 min. After that, during oxidation for 20 and 30 min, only a small increase in the functional groups amount was obtained. Efficiency of oxidative treatment with KMnO_4 significantly depends on pH, i.e. redox potential of the medium and present oxidizing chemical species. The higher values obtained in the case of permanganate oxidation for pH 11 is in accordance with literature indicating that permanganate ion (MnO_4^-), in aqueous alkaline media, is powerful oxidants and can react with hydroxyl groups in cellulose [3].

Table S1 Ratio of COOH and CHO groups in hemp fibers oxidized with KMnO₄, under different oxidative conditions, determined based on the area of the deconvoluted FTIR spectra, in the region 1685-1750 cm⁻¹, and determined by Ca-acetate method.

	Ratio of COOR, COOH and CHO groups						
	Before oxidation	After oxidation with Potassium permanganate					
Concentration, %		3			6		
pH value		7	9	11	7	9	11
Deconvolution, COOR/ (CHO + COOH)	16.31	-	-	-	-	-	-
COOR:CHO:COOH	-	3.1:1:3.4	2.3:1:3.0	1.9:1:2.8	2.0:1:3.0	1.2:1:3.0	0.8:1:2.4
Ca-acetate method, CHO:COOH	-	1:3.6	1:2.9	1:2.8	1:2.9	1:2.7	1:2.3

(S4) Capillary rise and wettability parameters D, C and R

Section Results and Discussion

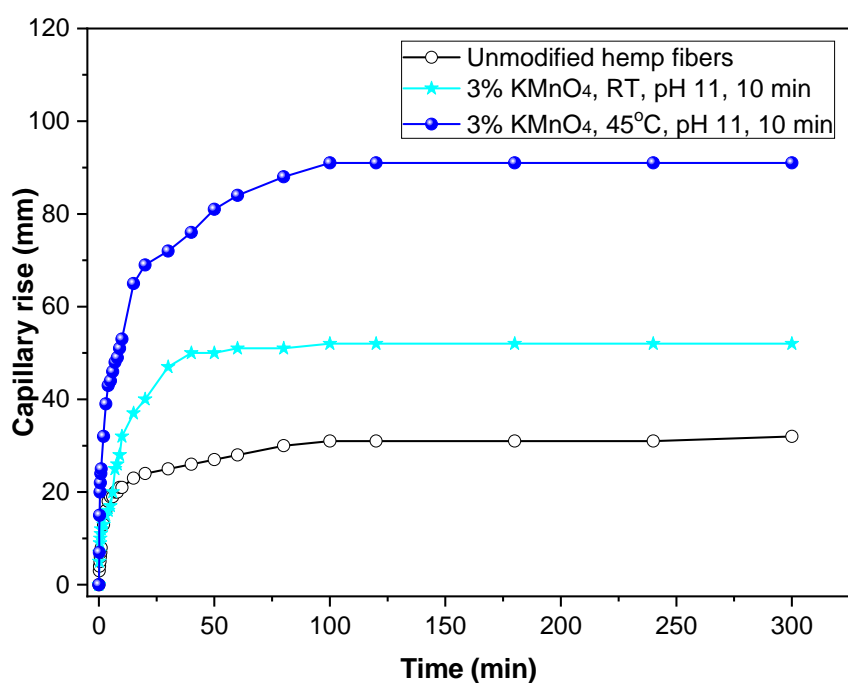


Figure S5 Capillarity rise of unmodified and hemp fibers oxidized with 3% KMnO₄, at pH 11 and 10 min, at room temperature and 45°C

In order to get more insight into the influence of mentioned changes on capillarity of modified hemp fibers, the wettability parameters (D, C and R) are calculated, using equations 2, 4 and 5 (in Supplementary S1), as slopes of corresponding graphs (**Figure S6**).

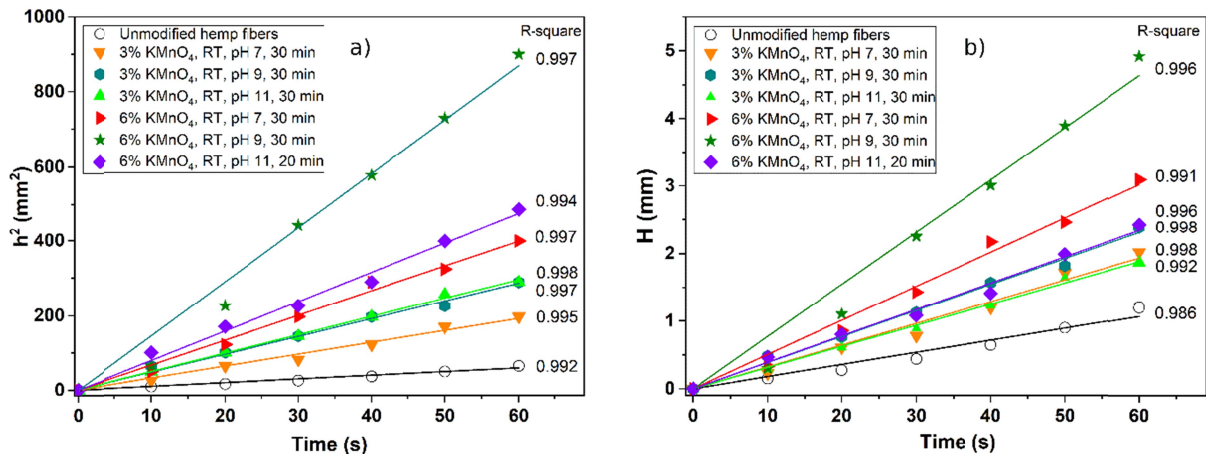


Figure S6 a) The influence of oxidative treatment on h^2 (Determination of coefficient D) and b) on H (Determination of coefficient C) for unmodified and set of oxidized hemp fibers

Figure S6a shows the dependence of h^2 -t. Since the coefficient of capillary diffusion D is affected by the oxidation with potassium permanganate, slopes of curves are changing with changing of oxidative parameters, and the value of coefficient D for oxidized hemp fibers increases in relation to the unmodified fibers. Measured for unmodified hemp fiber D is $0.9769 \text{ mm}^2\text{s}^{-1}$, and for oxidized hemp fibers, depending on oxidative conditions, it is from $1.139 \text{ mm}^2\text{s}^{-1}$ to $14.490 \text{ mm}^2\text{s}^{-1}$. The maximum value of $14.4901 \text{ mm}^2\text{s}^{-1}$ is obtained for sample oxidized with 6% KMnO₄, at pH 9 and room temperature, for 30 min. Obtained values of R_D^2 for most of the oxidized hemp fibers are greater than 0.99. According to calculated coefficients D, the values for samples treated at alkali pH (pH 9 and pH 11) have the higher values compared with D of samples oxidized in neutral medium (pH 7). Additionally, all samples oxidized for 30 min, have a higher value of coefficient D, compared to the D coefficient of samples oxidized for 10 and 20 min.

The influence of non-selective oxidation with KMnO₄ on capillary rise and coefficient D, is complex because, during oxidation, the different changes simultaneously occurs, and they together have an impact on capillarity. The coefficient of capillary diffusion D is affected by simultaneous removal of lignin and hemicelluloses, as well as structural changes

in hemp fibers. Mentioned changes alter the porous structure of hemp fibers and capillarity properties. The gradual removal of lignin, from the middle lamella, leads to fibrillation that induced new capillary spaces in an inter-surficial layer between completely or partially separated fibers within the technical modified hemp fiber. This effects together lead to faster liquid spreading in fibers facilitated by small, uniformly distributed and interconnected pores [1]. Comparing the results obtained for the Kappa number, as a measure of the presence of the lignin, and the value of the coefficient D for oxidized hemp fibers, a relation: a Kappa number decrease - the coefficient D increase, was observed, (for example: Kappa number: 22.63 – D: 1.140; Kappa number: 19.24 – D: 4.922).

On the other hand, the progressive removal of hemicelluloses located in the inter-fibrillar regions, during oxidative treatment, caused less dense and rigid the inter-fibrillar regions and thereby make the fibrils more capable to rearrangement [1]. According to the literature [4–6], 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.

For a better description, the coefficient C is determined because it is the coefficient related only to the size of the capillaries and to the nature of the liquid. Since the same liquid is used in all experiments the values for the viscosity, surface tension and density of the liquid are constants, the C is proportional to the square of the mean hydrodynamic radius of pores. Graphically shown, the coefficient C presents the slope of the graph H-t (**Figure S6b**). The results of coefficient C for oxidized hemp fibers are spread in a range from 0.0185 to 0.07730 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 oxidized hemp fibers, in relation to the unmodified fibers (0.0179 mm/s), is higher for all samples oxidized during 30 min, and in the case of oxidized samples with removed lignin.

The R values are in the range from 0.819–0.893, which confirm well enough the validity of assumption $\theta = \theta_{eq}$ in the case of wetting with eosin aqueous solution. Values of D, R_D -square, C, R_C - square and R for unmodified and oxidized hemp fibers are shown in **Figures S7, S8, S9**.

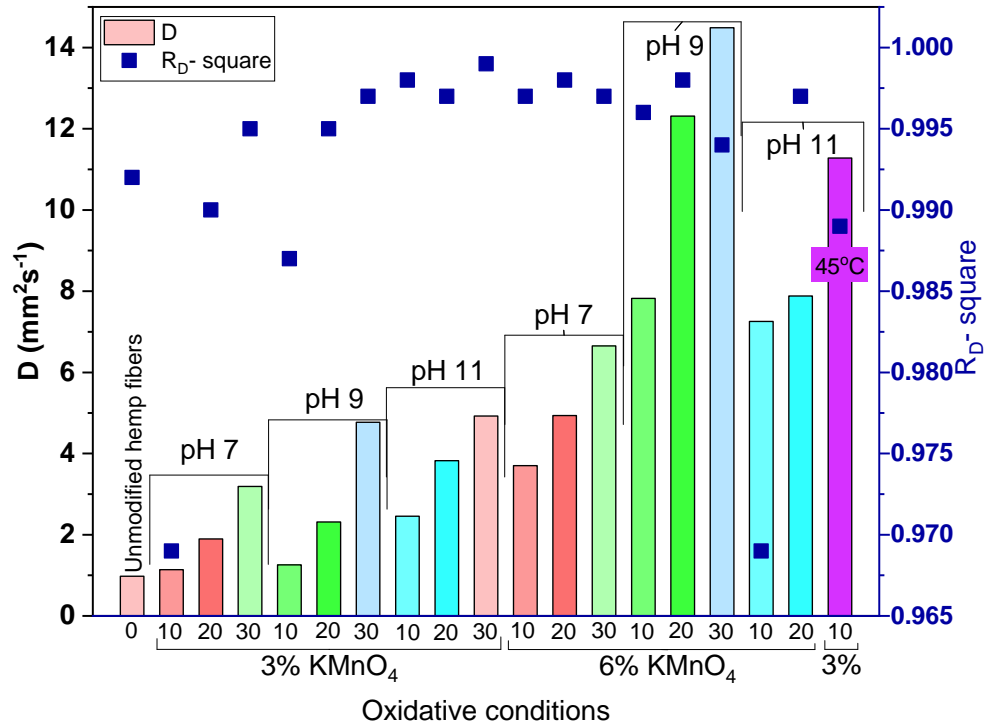


Figure S7 Values of coefficients D and R_D -square of unmodified and hemp fibers oxidized under different oxidative conditions

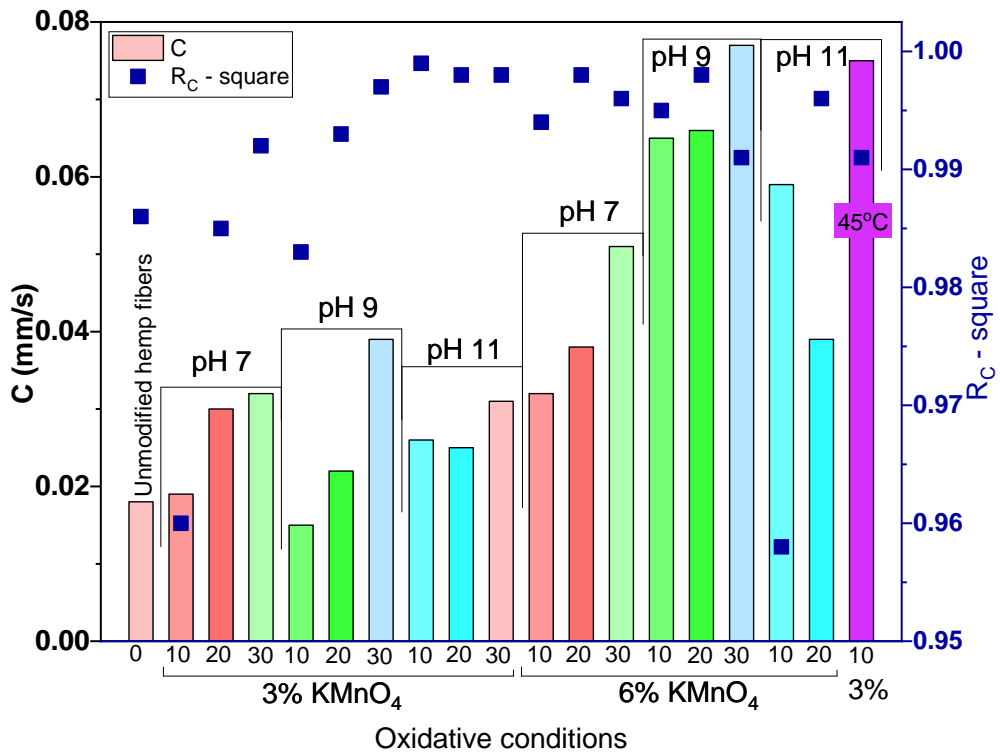


Figure S8 Values of coefficients C and R_C-square of unmodified and hemp fibers oxidized under different oxidative conditions

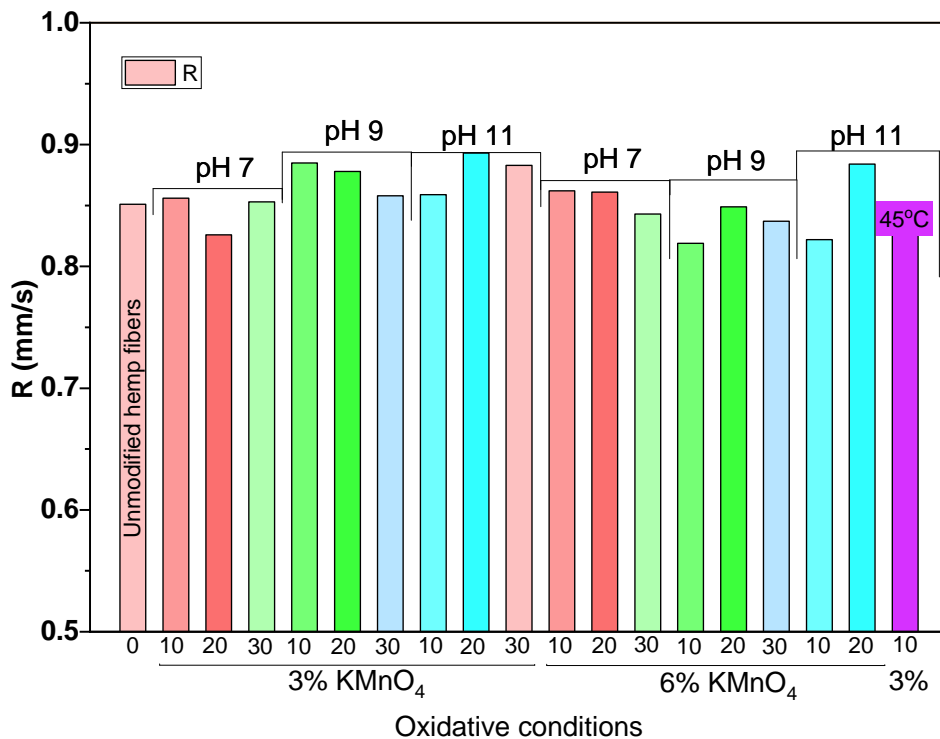


Figure S9 Values of coefficients R of unmodified and hemp fibers oxidized under different oxidative conditions

(S5) Mechanical properties – tenacity and elongation

Section Results and Discussion

During determination of tensile strength of hemp fibers, because of the variation in the hemp fibers fineness, as well as the fact that raw fibers stick into bundles, while oxidized fibers are mainly separated into single elementary cells (fibers), the tensile strength is expressed as tenacity, a specific value related to fineness (force per unit fineness). For such purposes, the fineness of every single fiber was determined before tensile testing.

Based on obtained results, that the oxidative process caused introduction of new functional groups, as well as the changes in hemp fiber fineness and chemical composition, due to the removal of non-cellulose components, primarily, the lignin removal, which joined elementary fiber bundles together, changes in mechanical properties of oxidized hemp fibers are expected. After oxidation with potassium permanganate, the reduced tenacity was obtained for all treated hemp fibers (**Figure S10**). The tenacity of hemp fibers oxidized at room temperature, with 3 % KMnO_4 , was decreased in the range from 18.60 cN/tex (sample modified at pH 7, during 10 min) to 4.2 cN/tex (sample modified at pH 11, during 30 min) and for samples oxidized with 6 % KMnO_4 from 12.2 cN/tex (sample modified at pH 7, during 10 min) to 3.1 cN/tex (sample modified at pH 11, during 20 min), compared to tenacity of unmodified hemp fibers (24.80 cN/tex). The obtained decrease can be explained, according to the literature [7], by considering that cement materials, rich in pectins, ensuring cohesion between fibers within an elementary fiber, were partially eliminated. Additionally, the lignin removal from middle lamella, that also binding the elementary fibers and microfibrils [8] and tenacity.

Sample oxidized under 45 °C with 3 % KMnO_4 , at room temperature, pH 7 and during 10 min, has the tenacity of 10.00 cN/tex. For more samples oxidized under 45 °C, the

fiber length obtained after oxidation was short and for these samples, it was not possible to determine tenacity. In some samples, significant changes in their structure and losing in fibrous structure occurred and it was not possible to measure the tenacity by the dynamometer (for example, samples modified with 6 % KMnO_4 , at a temperature of 45 °C and pH 11, longer than 20 minutes). Damage of modified fibers due to the application of rigorous oxidative conditions can be clearly seen in the SEM images shown in **Figure S11**.

Non-selective oxidation with potassium permanganate has no significant effect on the elongation of modified hemp fibers. Oxidation with KMnO_4 leads to a slight increase of elongation, from 5.30 % (samples modified with 3 % KMnO_4 , at room temperature and pH 7, during 20 and 30 minutes) to 7.55 % (sample modified with 6 % KMnO_4 , at room temperature and pH 7, during 20 minutes), compared to elongation for unmodified hemp fibers (5.02 %).

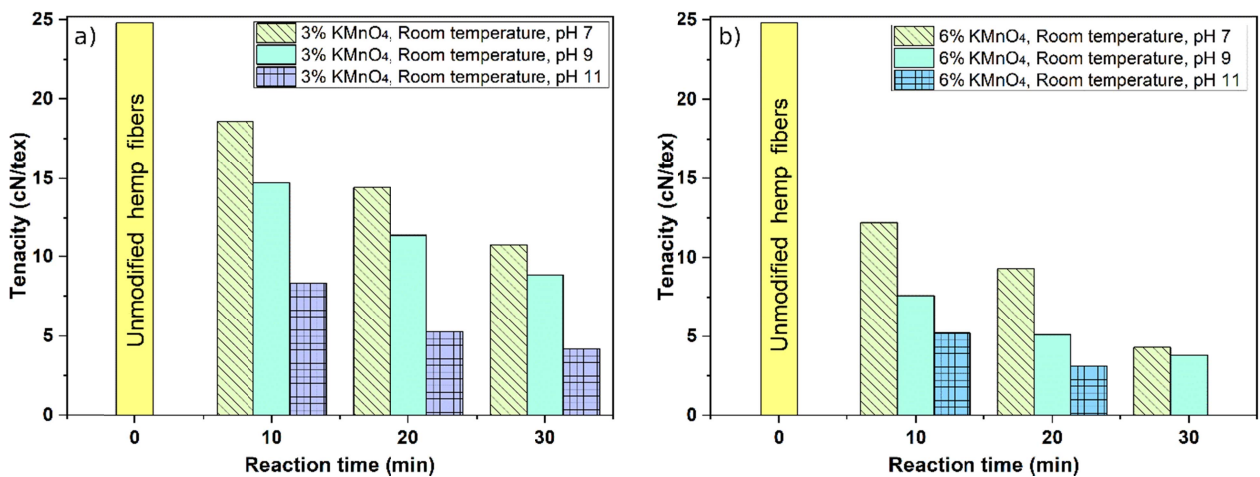


Figure S10 Tenacity of the hemp fiber oxidized with a) 3 % KMnO_4 and b) 6 % KMnO_4 during 10, 20 and 30 minutes, at room temperature at pH 7, 9 and 11.

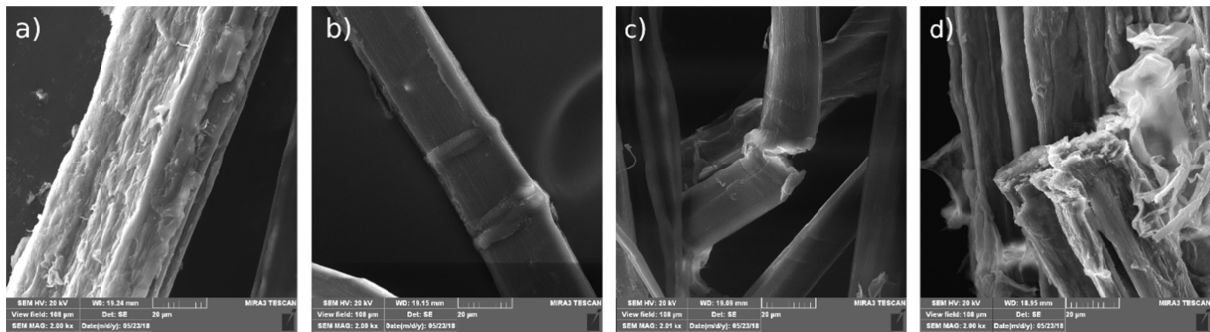


Figure S11 SEM images of a) unmodified hemp fibers and hemp fiber oxidized with b) 3 % KMnO_4 , at room temperature and pH 7, during 10 minutes; and sample modified with 6 % KMnO_4 , at 45 °C during 30 minutes at, c) pH 7 and d) at pH 11.

Reference:

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