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RESEARCH ARTICLE



## Influence of alkaline delignification time on the moisture uptake behaviour of hemp

Albert M. Manich<sup>a</sup> , Manuel J. Lis Arias<sup>b</sup> , Sonia Pérez-Rentero<sup>c</sup> , Marta Riba-Moliner<sup>d</sup> , Gabriela Mijas<sup>b</sup> , Meritxell Martí<sup>e</sup>  and Diana Cayuela<sup>b</sup> 

<sup>a</sup>Institute for Advanced Chemistry of Catalonia (IQAC-CSIC), Barcelona, Spain; <sup>b</sup>Textile Research Institute of Terrassa (INTEXTER), Universitat Politècnica de Catalunya, Terrassa, Spain; <sup>c</sup>“Josep Carilla” Thermal Analysis and Calorimetry Laboratory (IQAC-CSIC), Barcelona, Spain; <sup>d</sup>Materials Science and Engineering, Universitat Politècnica de Catalunya, Terrassa, Spain; <sup>e</sup>Cosmetic and Textile Innovations Group (IQAC-CSIC), Barcelona, Spain

### ABSTRACT

The influence of the alkaline delignification of hemp on its moisture uptake has been studied under the project “Preparation and functionalization of hemp for textile substrates” focussed on the reduction of cotton imports for the manufacturing of clothing, household textiles and medical devices. The project looks for the partial replacement of cotton by hemp on the production of natural cellulosic textiles. Hemp fibres are alkaline delignified at different times to evaluate its effect on their moisture uptake behaviour to evaluate the ability of replacing cotton in the next-to-skin goods manufacturing. The paper gives three easy tools to analyse the moisture uptake behaviour by determining the sorption ratio, the hysteresis and the parameters of the isotherms fitted using three different models (GAB, Hailwood-Horrobin and Dent) to the absorption/desorption isotherms. The samples of the original and delignified hemp have been subjected to moisture absorption/desorption trials from 5% to 95% RH at 25 °C. Sorption ratio and hysteresis reveal the greater influence of lignin on moisture uptake at low relative humidities, while at high, was cellulose which plays the most important role. The models fitted to the isotherms show that delignification decreases the size of the monolayer that, in desorption results always greater than in absorption. The energy constants of the monolayer for delignified fibres in absorption were higher than those for the original fibres, while the opposite occurred in desorption. Lignin caused great differences between absorption and desorption. The energy constants of the multilayer show a greater range of variation in delignified samples than in the original one, and results in absorption were higher than those in desorption. Delignification time of 3 h reached the highest cellulose content which best approached to the cellulose content of cotton causing that the moisture uptake behaviour drew near to it, especially at higher relative humidity.

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Hemp; alkaline delignification; moisture uptake behaviour; modelling; sorption ratio; hysteresis

## 1. Introduction

The increasing social demand for more sustainable manufacturing processes and the implementation of a circular economy founded on territorial clusters through agro-industrial symbiosis to reach a regenerative, climate-neutral and circular system for the industry, could be specifically come down in the textile industry, by reintroducing the cultivation of hemp to promote the production of textiles based on natural cellulosic fibres (Salmon-Minotte & Frank, 2005).

In 2016 the authors went on with the project “Preparation and functionalization of hemp for textile substrates” focussed on the reduction of cotton imports of the textile industry of its country for the manufacturing of clothing, household textiles and medical devices. The main objective was to look for the possibility of partial replacement of cotton by hemp on natural cellulosic textiles, considering the feasibility of reintroducing hemp cultivation as sustainable and biodegradable plant fibre.

Cultivation of hemp provides important ecosystem benefits while fostering economic development: bioremediation of heavy metal contaminated soils (Angelova et al., 2004; Grabowska & Baraniecki, 1997), reduction of greenhouse gas emissions and minimization of losses of natural resources and biodiversity. Hemp (*Cannabis sativa* L.) easily grows in a diversity of countries, habitats and climates around the world (Horne, 2020) and the ability of rooting deeply makes hemp a low nitrogen and irrigation demanding crop, leading to significant environmental benefits when compared with cotton.

Natural fibres obtained from annually renewable resources, coupled with the performance benefits is proving to have a strong appeal to consumers in various geographies.

Valuable hemp fibre can be obtained from the bast layer of hemp stalks that contains several coats of fibre bundles formed by a few unit cells (Sponner et al., 2005). The fibre can be considered a network of ultrafine cellulose fibrils embedded in a matrix of hemicelluloses and lignin (Pejic

et al., 2008). The cellulose content of hemp is lower than that of cotton (70–74%), and includes hemicelluloses (18–23%), pectin (0.9%), lignin (4–6%), water soluble substances and a certain amount of natural pigments (0.8%) (Shahzad, 2012).

Lignin creates mechanical incrustations inside of the amorphous cellulose and makes hemp stiffer, more breakable, and hinders their elementarisation and spinnability (Cierpucha et al., 2004). The objective of delignification is to obtain individual hemp fibres detached from fibre bundles by removing the lignin that holds them together. The predominant task in preparing hemp fibres for further processing is to remove non-cellulosic components, thereby improving sorption and other fibre properties without damaging cellulose in the fibre (Kostic et al., 2008). The “cottonized” hemp resulting from this process (Aishwarya Anand et al., 2018; Ciechanska & Nouisiaen, 2005) can be blended with cotton to spun yarns using the conventional short-staple spinning processes (Cierpucha et al., 2004; Sedelnik, 2004; Zhang & Zhang, 2010).

Lignin behaves as an easily accessible moisture-absorbing material that contributes to sorption *via* its carboxyl and both aliphatic and phenolic hydroxyl groups (Simon et al., 2017; Guo et al., 2016). When removed, causes significant alterations on the fibre surface and in accessibility (Yang et al., 2018). Delignification modifies fibre structure, chemical composition, crystallinity, mechanical properties and moisture uptake behaviour of hemp (Islam et al., 2010; Nilsson et al., 2005; Stevulova et al., 2014).

The influence of alkaline delignification on moisture uptake behaviour and bonding enthalpies of hemp was studied at the first step of the project, enabling to identify the contribution of the two main components of hemp, cellulose and lignin, that affect moisture management when external humidity changes (Manich et al., 2021).

The adequacy of the next-to-skin garments, household textiles and medical devices to the consumer, depends on fibre, yarn and fabric characteristic and properties, besides dyeing and finishing (Zhang & Zhang, 2010). Delignification, not only removes lignin from hemp, but also affects cellulose. Consequently, the characterization of the moisture uptake behaviour of the delignified fibres will enable the designers to identify how delignification contributes on the comfortability of a good that shall depend on both the application and the environmental conditions where it is planned to be used.

The moisture held within a cellulosic fibre, exerts a profound influence on its rheological properties (Morton & Hearle, 1986). When expressed as a fraction of the bone-dry weight of the fibres, moisture uptake is named as “moisture regain”  $X$ . The relation between moisture regain and relative humidity of the surrounding air at constant temperature describes the “sorption isotherm” that, in the case of cellulosic fibres, have a characteristic sigmoid shape Type II isotherm that at low relative humidities a moderate absorption of water occurs while at high humidities a considerable growth in absorption is done (Kneule, 1973). The relative humidity RH (%) can also be expressed as “water activity”  $a_w$

(RH/100), which agrees with the molar fraction of moisture content vs. moisture at saturation. If the relative humidity ranges from 0 to 100%,  $a_w$  will vary from 0 to 1. Desorption isotherm lies above the absorption one. This fact must be considered when conditioning fibres for rheological tests, by bringing them into equilibrium with a given relative humidity either along the absorption or along desorption curves because the final moisture uptake will be different.

Rheological tests are frequently made under controlled conditions of relative humidity and temperature, and it is useful to know the sorption isotherm for a particular material being investigated, so that the variation of the rheological property with regain, may be calculated from its variation with humidity. In addition to modifying the intrinsic properties of fibres, moisture absorption produces anisotropic swelling which alters the geometry of the fibre. Since in all fibres commonly used in textiles the molecules show a preferred orientation in the direction of the fibre axis and the crystallites are much longer than they are wide, the same thickness of non-crystalline fibre-water phase surrounding a crystalline region will produce greater swelling laterally than longitudinally. The changes in length and diameter with relative humidity show hysteresis, similar to the moisture regain (Meredith, 1956).

Based on the results of the absorption/desorption isotherm, two parameters can be easily determined to evaluate the effect of delignification on hemp.

- The sorption ratio, that compares the moisture uptake of delignified with that of the original one (Meredith, 1956), resulting in a constant that explains the mean loss in moisture uptake caused by delignification, and
- The hysteresis, that estimates the variation in moisture uptake in desorption,  $X_d$ , when compared with that in absorption,  $X_a$ , in percentage by  $H (\%) = 100 (X_d - X_a) / X_a$  (Okubayashi et al., 2004).

The moisture absorption/desorption isotherms of hygroscopic fibres can be fitted by different models (Arslan & Togrul, 2006; Furmaniak et al., 2009) being the most used those of Guggenheim, Anderson, and de Boer (GAB) (Timmermann, 2003), the Hailwood-Horrobin (Hill et al., 2009) and the Dent (1977) ones. All models yield the size of the monolayer, i.e. the amount of water strongly absorbed by the active sorption sites of the fibre (primary water), its energy constant that defines the initial convexity of the isotherm at low water activities, the energy constant of the multilayer that defines the concave shape at high water activities formed by the secondary water slightly bound to the primary water, that enables to estimate the regain at saturation and the level of water activity at which secondary water scores the primary one (Ussman et al., 2011). Table 1 summarises the different models of the absorption/desorption isotherms, the meaning of the parameters and the derived results that can be obtained from the models. The closer the moisture uptake behaviour of hemp to that of cotton used for the production of the next-to-skin goods, the greater the ability to replace it in this field.

**Table 1.** Summary of GAB, Dent and Hailwood-Horrobin isotherms of absorption/desorption, parameters and derived results.

Model	Mathematical equation
GAB	$X = X_m C K a_w / [(1 - K a_w)(1 - K a_w + C K a_w)]$
Dent <sup>1</sup>	$X = X_m b_0 a_w / [(1 - b a_w)(1 - b a_w + b_0 a_w)]$
H-H	$X = (1800/M) [K_1 K a_w / (1 - K_1 K a_w) + K a_w / (1 - K a_w)]$
Parameter	Definition
<u>Variable:</u>	
$a_w$	Water activity expressed as moisture relative pressure or molar fraction.
<u>Response:</u>	
$X$	Moisture uptake of the sample measured as regain (g of water / 100 g of bone-dry sample).
<u>Primary sorption:</u>	
$X_m$	Size of the monolayer as g of bonded water / 100 g of dry sample.
$M$	Molecular mass of the monohydrated sample (g mol <sup>-1</sup> )
$C$	Monolayer energy constant of the GAB model.
$b_0$	Monolayer energy constant of the Dent model.
$K_1$	Monolayer energy constant of the Hailwood-Horrobin model.
<u>Secondary sorption:</u>	
$K$	Multilayer energy constant of the GAB and Hailwood-Horrobin models.
$b$	Multilayer energy constant of the Dent model.
<u>Derived results:</u>	
$X_1$	Estimated regain at saturation ( $a_w=1$ )
$a_{w(\text{inf})}, X_{(\text{inf})}$	Water activity and regain where primary and secondary sorption are equal (GAB model)
$a_{w(p=s)}, X_{p=s}$	Water activity and regain where primary and secondary sorption are equal (HH & Dent models)

### 1.1. Objective

The objective of this work is to study the effect of the time of alkaline delignification on the moisture uptake behaviour of hemp, by the application of three tools on the analysis of the absorption desorption isotherms: a) sorption ratio, b) hysteresis and c) parameters of the isotherms fitted using three different models.

The parameters derived from the fitted isotherms are the size of the monolayer, the energy constants of both primary and secondary sorption, enabling to estimate the moisture uptake at saturation and the level of water activity and regain at which secondary water scores the primary one.

### 1.2. Novelty and justification of the work

As mentioned in the introduction, the work has been done under the project “Preparation and functionalization of hemp for textile substrates” to study the ability of hemp in replacing cotton in clothing, household textiles and medical devices to reduce cotton import, by estimating its moisture uptake behaviour.

The technological feasibility of this replacement has been demonstrated at pilot-plant level by blending delignified hemp with cotton producing drawn slivers 20/80 and 40/60 hemp/cotton blends that have been spun by an open-end rotor spinning unit to produce 40 tex yarns. The optimization of the spinning process and spun yarn properties will be considered elsewhere.

This paper is focussed on the estimation of the ability of delignified hemp to replace cotton by the characterization of its moisture uptake looking for closer similarity to that of cotton, to evaluate its adequacy to be included in the manufacturing of goods close-to-skin like clothing, household textiles and medical devices.

The novelty of the paper lies on the application of three tools that easily characterise the moisture uptake behaviour, that can be extended to other lignocellulosic fibres:

- determination of the sorption ratio defined more than 60 years ago (Meredith, 1956),
- determination of the hysteresis that combined with sorption ratio, enables to identify the levels of humidity where lignin or cellulose play the most influencing role on moisture uptake, and
- determination of the size of the monolayer and the energy constants of primary and secondary sorbed water, by fitting the three most used models (GAB, Hailwood-Horrobin and Dent) to the absorption/desorption isotherms.

By these tools it has been possible to evaluate the effect of the time of alkaline delignification and, consequently the contribution of lignin on the moisture uptake and the different behaviour between absorption and desorption, confirming that the desorption isotherm is the most adequate to characterize the effect of delignification on moisture uptake behaviour of hemp.

## 2. Materials

### 2.1. Original hemp

The raw hemp fibres, were supplied by CELESA (Celulosa de Levante, S.A., from Tortosa, Spain) that supplies hemp for the production of different types of paper. The fibre length of the hemp ranged from 5 to 55 mm and fineness was between 16 to 50 µm. This type of hemp was used because of the lack of hemp for textile production at the beginning of the project. Hemp was rinsed in distilled water at room temperature for 10 min to remove impurities, dust,

and salts soluble in water, and the resulting fibres were used as the original raw material.

## 2.2. Delignified hemp

The original hemp fibres were subjected to an alkaline delignification treatment under the following conditions: NaOH ( $40 \text{ g L}^{-1}$ ), Hostapal DTC surfactant ( $1.5 \text{ g L}^{-1}$ ), temperature of  $110^\circ\text{C}$ , three different times (2, 3 and 4 h), and bath ratio 1:20. The samples were then rinsed with distilled water at  $80^\circ\text{C}$  and subjected to neutralisation treatment with acetic acid. Two final rinses with distilled water were applied. After drying, delignified hemp was obtained.

## 3. Methods

### 3.1. Lignin content

The lignin content was chemically determined according to the TAPI T222 om-15 standard. The results were correlated with those obtained by thermogravimetry (TGA), and the lignin content in % was determined according to procedures described elsewhere (Cayuela et al., 2019).

### 3.2. Moisture absorption/desorption trials

Moisture absorption/desorption isotherms were performed at  $25^\circ\text{C}$  on samples of approximately 10 mg using a Q5000 dynamic vapour sorption DVS analyser (TA Instruments) according to the following procedure:

1. Initial drying at  $60^\circ\text{C}$  and 0% relative humidity for 300 min.
2. Prestabilisation at 0% relative humidity and  $25^\circ\text{C}$  and then, at a relative humidity RH of 5% until stabilisation was achieved.
3. Absorption process: The sample stabilised at 5% RH was subjected to increasing absorption stages until stabilisation was reached, with RH increasing from 15% to 25%, 35%, 45%, 55%, 65%, 75%, 85% and 95%.
4. Desorption process: Samples stabilised at 95% RH were subjected to decreasing desorption stages, with RH decreasing to 85%, 75%, 65%, 55%, 45%, 35%, 25%, 15% and 5%, to complete a cycle of moisture absorption/desorption.
5. The maximum time that the samples remained at each absorption/desorption stage was 500 min. This time was shortened if the quasi-stabilisation conditions were reached (variation in sample mass lower than 0.01% for 18 minutes). In that case, the sample proceeds to the next stage.

### 3.3. Sorption ratio

Using the experimental results of regain given by the absorption/desorption trials, the sorption ratio between delignified hemp at different times and raw hemp according to different water activities  $a_w$  from 0.05 to 0.85, during

absorption and desorption were determined. The effect of measuring conditions (water activity and absorption/desorption) and time of delignification on the sorption ratio between delignified and original hemp was determined by analysis of variance (Mead et al., 2003).

### 3.4. Hysteresis

The experimental results of regain of the samples at different levels of water activity from 0.05 to 0.85 enabled us to calculate the hysteresis,  $H (\%) = 100 (X_d - X_a)/X_a$ , being  $X_d$  the regain in desorption and  $X_a$  the regain in absorption at the same level of water activity. The effect of water activity on the original and delignified hemp samples was determined by analysis of variance (Mead et al., 2003).

### 3.5. Fitting the isotherms of moisture absorption/desorption

The software of the Q5000 dynamic vapour sorption DVS analyser (TA Instruments) automatically gave the parameters of the GAB absorption isotherm giving the size of the monolayer  $X_m$ , the monolayer energy constant  $C$ , the multi-layer energy constant  $K$  and the determination coefficient  $R^2$ .

The results automatically given by the DVS were used as initial estimators of the nonlinear regression procedure described elsewhere (Manich et al., 2017), that enables to get the parameters of the best fitted absorption and desorption isotherms (Draper & Smith, 1981). Based on the fitted absorption isotherm the moisture uptake at saturation  $X_I$  was calculated ( $a_w = 1$ ). To get the desorption isotherm,  $X_I$  and the values of regain in desorption from  $a_w = 0.85$  to  $a_w = 0.05$  were used. The initial estimators for the nonlinear regression procedure to get the model in desorption were the same used in absorption.

The initial estimators to apply the nonlinear regression procedure to get the Hailwood-Horrobin and the Dent models were yielded either by transforming the initial estimators of the DVS for the GAB model to their equivalents through the relations explained elsewhere (Manich et al., 2021) or using the procedures described for the Hailwood-Horrobin (Hill et al., 2009) and Dent (1977) models. The application of the same iterative nonlinear regression procedure enabled to get the best fitted models for absorption, which were used to predict the maximum regain,  $X_I$  at  $a_w = 1$  and, as was done for the GAB model,  $X_I$  and the results in desorption from  $a_w = 0.85$  to  $a_w = 0.05$  lead to the best fitted Hailwood-Horrobin and Dent models in desorption. The goodness of fit was estimated by the determination coefficient adjusted to the degrees of freedom,  $R^2_{adj}$ .

## 4. Results and discussion

### 4.1. Lignin content

The lignin content of the original hemp was 6.2% while those of the alkaline delignified for 2, 3 and 4 h were respectively 3.2%, 2.9% and 3.0%.

### 4.2. Absorption/desorption isotherms

Table 2 shows the results of regain,  $X$  (% in bone-dry weight), reached at the end of each stage of absorption for water activity values of 0.05 to 0.95 and at the end of each stage of desorption for water activity values from 0.85 to 0.05 for the raw hemp (OR) and alkaline delignified hemp according to the delignification time: 2 U (2 h), 3 U (3 h) and 4 U (4 h).

### 4.3. Sorption ratio

Based on the experimental results of Table 2, the sorption ratio between the delignified hemp at different times and the original hemp was determined according to the water activity at which the samples were stabilised, from 0.05 to

**Table 2.** Regain  $X$  of the samples of the Original (OR) and the delignified hemp during 2, 3 and 4 h (2U, 3U, 4U respectively) when the stabilization conditions are reached, following a cycle of absorption and desorption according to the different levels of water activity  $a_w$  at 25°C.

Sample reference	OR / % odw	2U / % odw	3U / % odw	4U / % odw
$a_w$ levels in Absorption:				
0.05	1.110	0.910	0.897	0.885
0.15	2.832	2.199	2.146	2.170
0.25	4.179	3.209	3.128	3.169
0.35	5.415	4.133	4.018	4.084
0.45	6.642	5.069	4.898	4.987
0.55	8.013	6.081	5.869	5.986
0.65	9.569	7.312	7.067	7.191
0.75	11.65	8.963	8.694	8.913
0.85	14.85	11.45	11.15	11.48
0.95	21.43	17.11	16.50	17.05
$a_w$ levels in Desorption:				
0.85	16.40	13.48	13.13	13.43
0.75	13.36	10.88	10.65	10.84
0.65	11.24	8.995	8.816	9.011
0.55	9.699	7.635	7.426	7.513
0.45	8.282	6.349	6.179	6.263
0.35	6.929	5.243	5.076	5.144
0.25	5.593	4.128	4.010	4.035
0.15	4.077	2.964	2.843	2.878
0.05	2.085	1.492	1.458	1.431

**Table 3.** Sorption Ratio between regains of delignified and raw hemp fibres, according to water activity  $a_w$ , time of delignification and the way used to reach stabilisation (absorption or desorption).

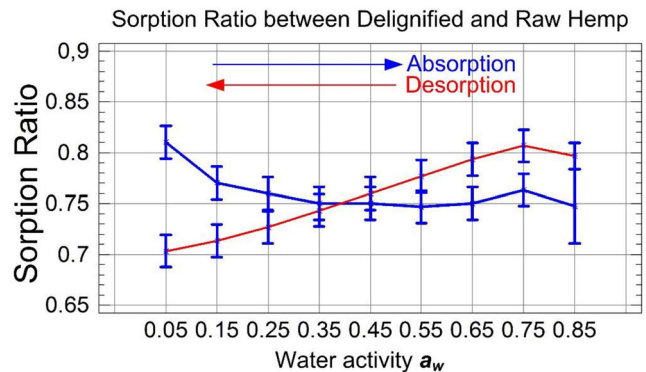
$a_w$	Sample 2U (2 h)		Sample 3U (3 h)		Sample 4U (4 h)	
	Absorption	Desorption	Absorption	Desorption	Absorption	Desorption
0.05	0.82	0.72	0.81	0.70	0.80	0.69
0.15	0.78	0.73	0.76	0.70	0.77	0.71
0.25	0.77	0.74	0.75	0.72	0.76	0.72
0.35	0.76	0.76	0.74	0.73	0.75	0.74
0.45	0.76	0.77	0.74	0.75	0.75	0.76
0.55	0.76	0.79	0.73	0.77	0.75	0.77
0.65	0.76	0.80	0.74	0.78	0.75	0.80
0.75	0.77	0.81	0.75	0.80	0.77	0.81
0.85	0.77	0.82	0.75	0.80	0.77	0.82

0.85, and the method of stabilisation (absorption or desorption). The results are shown in Table 3.

The application of analysis of variance using a standard statistical software (Statgraphics Plus 5, 5, 2000) to the results of Table 3 allowed us to evaluate the effect of the delignification time, water activity and method of stabilisation (absorption/desorption) on this parameter. The mean sorption ratio of the samples delignified for 2, 3 and 4 h were respectively 0.769, 0.751 and 0.758. No significant differences were observed between those delignified for 3 and 4 h, while the mean sorption ratio of the delignified for 2 h was significantly higher than the other two. A significant interaction between the water activity and the way the samples were stabilized (absorption or desorption) was observed and is shown in Figure 1.

Moisture comes into dry fibres, and although delignification reduced lignin by more than 50%, the remaining lignin played a significant role in absorbing free moisture coming from the environment at low water activities, starting with a high sorption ratio (0.81) that decreases as water activity grows. When  $a_w$  exceeded 0.25, the sorption ratio remained at approximately 0.75, which can be attributed to the role of the cellulose in moisture uptake.

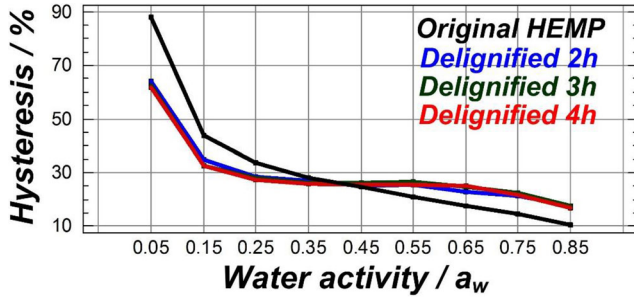
When desorption began, the sorption ratio was significantly higher than that during absorption. The differences can be explained by the structural and conformational rearrangements caused by the presence of water in the fibre, which altered the accessibility of energetically polar sites (Heldman et al., 1965). Moisture sorption and desorption are in dynamic equilibrium, and time enables water molecules to progressively reach inner sorption sites, enabling the completion of monolayers and the growth of secondary multilayers. In desorption, the secondary sorbed molecules near the external surface that were weakly linked to lignin were the first to go out to the environment, being followed by the more internal secondary water, the flow of which progressively decreases as moisture was removed (Manich et al., 2010). The sorption ratio in desorption decreases with the reduction of water activity. Delignification decreases the sorption ratio of hemp at 0.759 (0.761 in absorption and 0.758 in desorption), with no significant differences between them.



**Figure 1.** Mean values of sorption ratio including confidence intervals at 95% between alkaline delignified hemp during 2, 3 and 4 hours and the original hemp as a function of the water activity and the method of stabilization (absorption/desorption).

**Table 4.** Hysteresis of the original and delignified hemp at 2, 3 and 4 h according to the different levels of water activity  $a_w$  in %.

$a_w$	Original / %	Delig. 2 h / %	Delig. 3 h / %	Delig. 4 h / %
0.05	87.84	63.99	62.49	61.69
0.15	43.96	34.79	32.48	32.63
0.25	33.84	28.64	28.20	27.33
0.35	27.96	26.86	26.33	25.95
0.45	24.69	25.25	26.15	25.59
0.55	21.04	25.56	26.53	25.51
0.65	17.46	23.02	24.75	25.31
0.75	14.68	21.39	22.50	21.62
0.85	10.44	17.73	17.76	16.99

**Figure 2.** Hysteresis of the delignified and original hemp in function of the water activity.

#### 4.4. Hysteresis

The application of the equation given in section 3.4 to the results of Table 2 enabled the determination of hysteresis by comparing regain in desorption to that in absorption for the original and delignified hemp samples for 2, 3 and 4 h according to the levels of water activity from 0.05 to 0.85. Results are shown in Table 4.

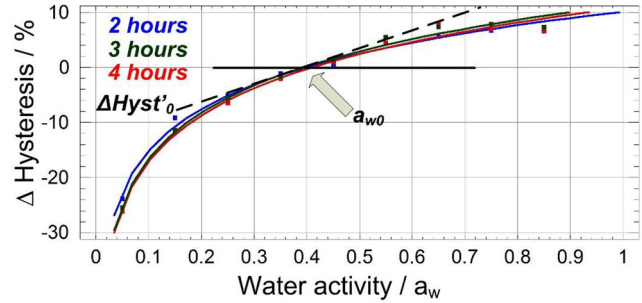
The analysis of variance shows that delignification decreased hysteresis at water activities lower than 0.40, while at higher values, hysteresis of the delignified samples remained above of the original untreated hemp. Hysteresis was also greatly influenced by water activity. The highest values were caused by the water directly linked to the polymer (low water activity), and as water activity increases, hysteresis gradually decreases, reaching the lowest values at the highest water activity. Figure 2 shows the results according to  $a_w$  and delignification time.

Hysteresis seems to be due to the hydroxyl groups taking part in absorption and desorption, which are modified by swelling caused by water uptake, that also modifies the physical state and properties of the fibre. Delignification reduces hysteresis, probably because of the loss of free hydroxyl groups of wood that fix water by hydrogen bonds (Guo et al., 2016). Figure 2 suggests that lignin could play a prominent role in hysteresis at low water activities, while cellulose played a strong role at high water activities.

The estimation of the reduction in hysteresis caused by delignification of the original hemp can be done through the calculation of the mean value of the Manhattan distance,  $Md$ , based on the absolute differences in hysteresis,  $\Delta Hyst = |Hyst_{delign} - Hyst_{original}|$ , for all water activities. The greater the mean distance is, the stronger the effect of delignification. Differences in hysteresis caused by delignification as a

**Table 5.** Mean Manhattan distance  $Md$ , and parameters A and B of the model including C.I. at 95% that fits the difference in hysteresis caused by delignification  $\Delta Hyst$  in function of water activity  $a_w$ ,  $\Delta Hyst = A + B \text{ LOG}(a_w)$  according to the time of delignification. Water activity at which hysteresis of delignified hemp is equal to that of the original one  $a_{w0}$ , slope at this point  $\Delta Hyst'_0$  and determination coefficient  $R^2$ .

Delign. time	$Md$ (%)	A (%)	B	$a_{w0}$	$\Delta Hyst'_0$ (%)	$R^2$ (%)
2 h	$7.11 \pm 0.44$	$10.09 \pm 1.20$	$10.98 \pm 0.87$	0.399	27.53	99.61
3 h	$8.16 \pm 0.44$	$11.32 \pm 1.33$	$12.14 \pm 0.97$	0.394	30.84	99.21
4 h	$8.08 \pm 0.44$	$10.82 \pm 1.70$	$12.14 \pm 1.24$	0.410	29.59	98.71

**Figure 3.** Loss in hysteresis caused by delignification.

function of water activity,  $a_w$ , were fitted by the equation  $\Delta Hyst = A + B \text{ LOG}(a_w)$ , where A is the estimation of  $\Delta Hyst$  at saturation ( $a_w = 1$ ) and B is the growth rate of  $\Delta Hyst$  as a function of the logarithm of water activity. The equation allowed for the determination of the value of  $a_w$  at which hysteresis values of the original and delignified hemp samples are the same ( $\Delta Hyst = 0$ )  $a_{w0}$ . The derivative of this function,  $\Delta Hyst'_0$ , at  $a_{w0}$  gave the growth rate of the loss in hysteresis at  $a_{w0}$ ,  $\Delta Hyst'_0$ , caused by delignification. Table 5 shows the results of the function, including the determination coefficient,  $R^2$ , as an estimator of the goodness of fit, and the results are plotted in Figure 3. The greater the values of  $Md$  and  $\Delta Hyst'_0$  are, the larger the differences between the delignified and original hemp samples. Hemp delignified for 2 h showed the lowest Manhattan distance, the smallest difference in hysteresis at saturation, the shortest growth rate vs. water activity and the value of water activity at which no differences in hysteresis between original and delignified hemp was observed. Hemp delignified for 3 and 4 h showed greater values for these parameters, and no significant differences between them were observed.

#### 4.5. Fitting the isotherms of absorption/desorption

The different models of absorption/desorption were fitted to the results of Table 2 using the procedures described in paragraph 3.5, and Tables 6–8 shows the results of GAB, Hailwood-Horrobin and Dent models respectively, yielding all of which the size of the monolayer, the energy constants of primary and secondary absorption, the goodness of fit measured by the determination coefficient adjusted for the degrees of freedom, the maximum regain at saturation, and the levels of water activity and regain at which primary and secondary sorption reach the same level.

Regression analysis of the estimators given by the three models allowed for the identification of the relationship

**Table 6.** GAB model. Parameters of the absorption and desorption isotherms at 25°C of original (OR) and delignified samples for 2 h (2U), 3 h (3U) and 4 h (4U): Monolayer size  $X_m$ , energy constants of the monolayer  $C$  and the multi-layer  $K$ , determination coefficient of the model  $R^2_{adj}$ , regain at saturation  $X_1$  (% odw), water activity  $a_{w(inf)}$  and regain  $X_{(inf)}$  at the inflection point of the isotherm where primary and secondary absorption are equal.

Reference	$X_m$ /%	$C$	$K$	$R^2_{adj}$ /%	$X_1$ /%	$a_{w(inf)}$	$X_{(inf)}$ /%
<b>Absorption isotherm:</b>							
OR	4.91	8.20	0.818	99.86	26.20	0.305	4.786
2U	3.59	9.22	0.836	99.82	21.41	0.299	3.607
3U	3.49	9.21	0.834	99.87	20.63	0.300	3.512
4U	3.55	8.98	0.838	99.88	21.44	0.298	3.547
<b>Desorption isotherm:</b>							
OR	5.93	13.33	0.777	99.87	26.20	0.316	6.389
2U	4.87	9.54	0.779	99.96	21.41	0.321	4.937
3U	4.83	8.99	0.773	99.96	20.63	0.323	4.824
4U	4.86	8.90	0.780	99.96	21.44	0.321	4.851

**Table 7.** Hailwood-Horrobin model. Parameters of the absorption and desorption isotherms at 25°C of original (OR) and delignified samples for 2 h (2U), 3 h (3U) and 4 h (4U): Molecular mass of the monohydrated sample ( $M$  g mol<sup>-1</sup>), equilibrium constant of the primary  $K_1$  and the secondary  $K$  absorption, regain at saturation  $X_1$  (% odw), determination coefficient of the model  $R^2_{adj}$ , water activity  $a_{w(p=s)}$  and regain  $X_{(p=s)}$  at which both the primary and the secondary absorption are equal.

Reference	$M$ /g mol <sup>-1</sup>	$K_1$	$K$	$X_1$ /%	$R^2_{adj}$ /%	$a_{w(p=s)}$	$X_{(p=s)}$ /%
<b>Absorption isotherm:</b>							
OR	366.6	7.20	0.818	26.20	99.86	0.527	7.427
2U	501.9	8.21	0.836	21.41	99.82	0.525	5.616
3U	515.9	8.21	0.834	20.63	99.87	0.526	5.463
4U	506.7	7.97	0.838	21.44	99.88	0.522	5.521
<b>Desorption isotherm:</b>							
OR	303.5	12.32	0.777	26.20	99.87	0.591	10.081
2U	369.8	8.54	0.779	21.41	99.96	0.567	7.694
3U	372.7	7.99	0.773	20.63	99.96	0.566	7.510
4U	370.3	7.90	0.780	21.44	99.96	0.560	7.536

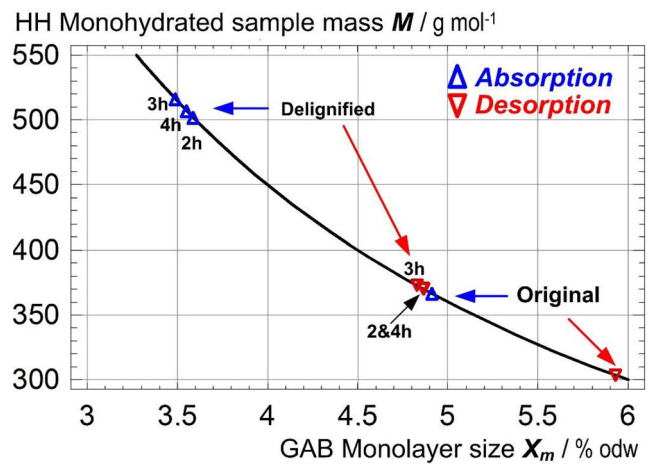
**Table 8.** Dent model. Parameters of the absorption and desorption isotherms at 25°C of original (OR) and delignified samples for 2 h (2U), 3 h (3U) and 4 h (4U): Monolayer size  $X_m$ , energy constants of the monolayer  $b_0$  and the multi-layer  $b$ , regain at saturation  $X_1$  (% odw), determination coefficient of the model  $R^2_{adj}$ , water activity  $a_{w(p=s)}$  and regain  $X_{(p=s)}$  levels where both the primary and the secondary absorption are equal.

Reference	$X_m$ /%	$b_0$	$b$	$X_1$ /%	$R^2_{adj}$ /%	$a_{w(p=s)}$	$X_{(p=s)}$ /%
<b>Absorption isotherm:</b>							
OR	4.81	6.70	0.818	25.67	99.86	0.612	8.578
2U	3.59	7.70	0.836	21.41	99.82	0.598	6.471
3U	3.49	7.68	0.834	20.63	99.87	0.599	6.295
4U	3.55	7.52	0.838	21.44	99.88	0.597	6.392
<b>Desorption isotherm:</b>							
OR	5.93	10.36	0.777	25.67	99.87	0.643	11.034
2U	4.87	7.45	0.779	21.41	99.96	0.642	8.811
3U	4.83	6.95	0.773	20.63	99.96	0.647	8.692
4U	4.86	6.94	0.780	21.44	99.96	0.641	8.739

between these parameters, that were grouped according to the significance of their relationships.

#### 4.5.1. Monolayer size

The monolayer of delignified hemp was significantly smaller than that of the original hemp. Estimations obtained through the GAB and Dent models led to very similar results for delignified hemp regardless of the delignification time, resulting identical in desorption. The size of the monolayer  $X_m$ , measured in g of water bonded to 100 g of bone-dry sample is related to the molecular mass  $M$ , of the



**Figure 4.** Relationship between monolayer size and molecular mass of the monohydrated sample.

monohydrated sample given by the Hailwood-Horrobin model through equation  $M = 0.0178 + 1799.92/X_m$ , with a correlation coefficient  $r = 1.00$ , as shown in Figure 4.

The size of the monolayer measured during desorption was always higher than the results measured during absorption. Lignin greatly contributed to the increase in the size of the monolayer. The lowest values were those measured for delignified samples in absorption, and the greatest was the value measured for the original sample in desorption. Intermediate results were given by both the delignified samples during desorption and the original sample during absorption. Regarding the effect of delignification time, the results given by samples delignified for 2 h show a very weak increase in the size of the monolayer, although no clear effect of delignification time on the size of the monolayer was determined in this particular range of time, from 2 to 4 h.

In absorption, the hindering effect of primary sorbed molecules difficult the completion of the innermost reactive sites of the fibre. At the beginning of absorption, a large amount of water links the less hydrophilic lignin and exterior cellulose sites, favouring secondary sorption to these sites, which explains the lower regain and monolayer size values. In desorption, the contrary occurs: water linked to lignin and all secondary water are easily removed, which explains the higher estimations of regain and monolayer size.

#### 4.5.2. Energy constants of the monolayer

The energy constants of the monolayer for the three models were highly related. The linear regression and correlation coefficients among the model energy constants of the monolayers shown in Figure 5 are as follows:

GAB $C$ and Hailwood-Horrobin $K_1$ :	$K_1 = C - 1$	( $r = 1.00$ )
GAB $C$ and $b_0$ Dent:	$b_0 = 0.84 + 0.71 C$	( $r = 0.98$ )
Hailwood-Horrobin $K_1$ and $b_0$ Dent:	$b_0 = 1.56 + 0.71 K_1$	( $r = 0.98$ )

Lignin causes great differences between absorption and desorption when the energy constant of the monolayer is measured, as the extreme values correspond to original hemp. Regarding delignified hemp, the monolayer constants

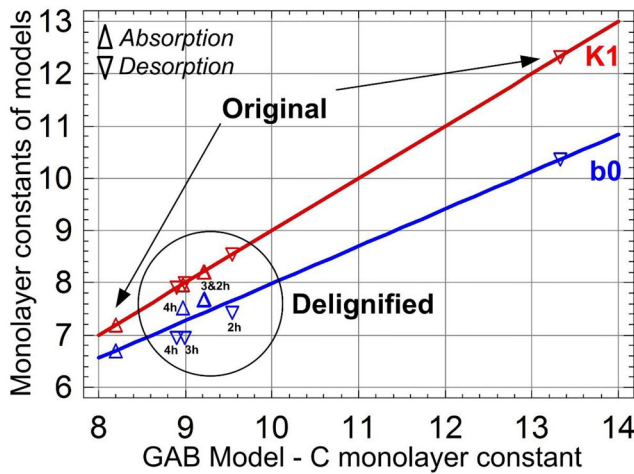


Figure 5. Relationship between the monolayer energy constants of the GAB, Hailwood-Horrobin and Dent models.

were closer to those of the original sample measured in absorption. Although the delignification time does not significantly affect the monolayer energy constant, it can be observed that the greater the time was, the lower the constant. Differences between constants measured in absorption and desorption were inconsistent for  $C$  and  $K_I$ ; consequently, they were not significant, while for  $b_0$ , the results obtained in desorption were systematically lower than those obtained in absorption, reaching a slight level of significance of 10%, showing the opposite behaviour clearly observed in the original hemp.

#### 4.5.3. Energy constant of the multilayer and regain at saturation

The energy constants of the multilayer were identical for the three models, showing a greater range in variation in delignified samples than in the original sample. The absorption results (0.831) were significantly higher than those obtained during desorption (0.777), and although the effect of time was unclear, the sample delignified for 4 h during absorption exhibited the highest constant (0.838), and the sample delignified for 3 h during desorption exhibited the lowest constant (0.773).

Delignification caused a decrease in regain of approximately 5.7% at saturation, and the effect of delignification time on this parameter was not clear. The highest regain at saturation was observed for the original sample (26.1%), while the lowest regain was observed in the sample delignified for 3 h (20.6%), being significantly greater the regain of the samples delignified for 2 and 4 h (21.4%).

#### 4.5.4. Water activities at which primary and secondary moisture uptake values are equal

The water activity at which the primary and secondary moisture uptake were the same, i.e. secondary water scored the primary one, depends on the model used: the lowest values were those given by the GAB model because its estimation was based on the inflection point of the isotherm. Higher results were given by the Hailwood-Horrobin model, and the

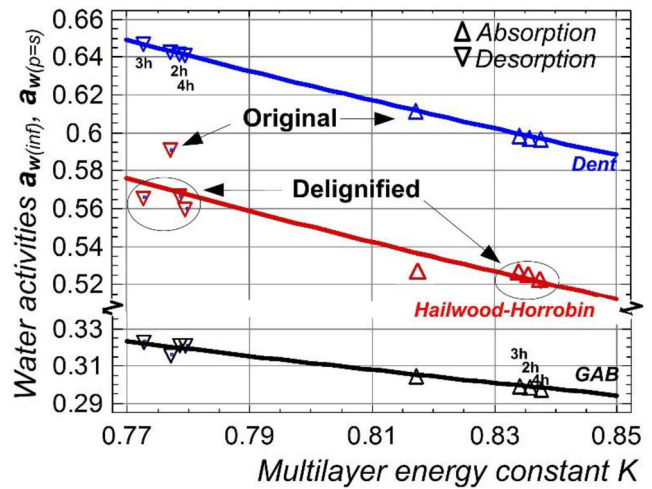


Figure 6. Relationship between multilayer energy constant and water activity at which primary and secondary sorption are equal.

highest results were those of the Dent model. The estimations of these two last models depend on the way they split primary and secondary moisture uptake values, resulting in different levels of water activity at which both the primary and secondary moisture uptake values were equal.

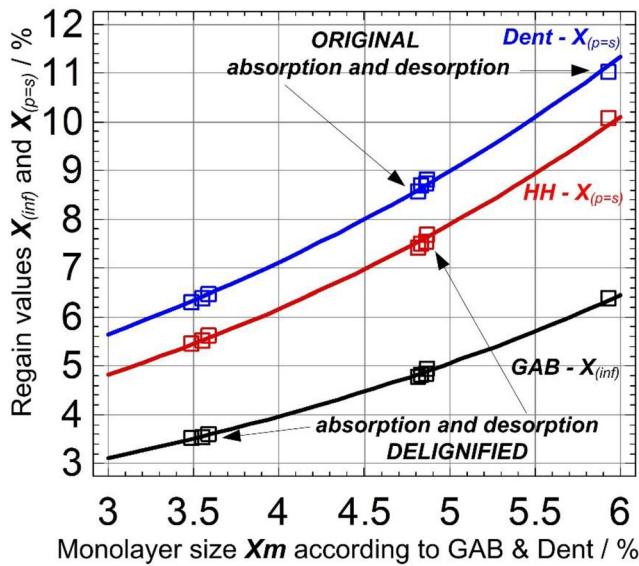
A very strong relationship between these water activities and the energy constant of the multilayer (secondary sorption) was observed, so the greater the constant was, the lower the water activity at which primary uptake was equal to secondary uptake. Figure 6 shows these results according to the different models as a function of the energy constant of the multilayer.

The original hemp in absorption shows a significantly lower multilayer constant (0.818) than the delignified samples (0.835), while in desorption, the difference between original and delignified samples can be detected through the water activity,  $a_{w(p=s)}$ , as determined by the Hailwood-Horrobin results of the original sample (0.591) being greater than those of the delignified samples (0.564). Differences between the multilayer constants of the original and delignified samples during desorption were irrelevant between 0.780 and 0.773.

The water activity at which primary sorption is equal to secondary sorption,  $a_{w(p=s)}$ , according to the Dent and Hailwood-Horrobin models, led to higher values than those determined by the GAB model,  $a_{w(\text{inf})}$ . The best correlations with the multilayer energy constant,  $K$ , are those given by the Dent and GAB models, followed by those of the Hailwood-Horrobin model:

Dent model:	$a_{w(p=s)} = 1/(1.9956 K + 0.0036)$	( $r = 1.00$ )
GAB model:	$a_{w(\text{inf})} = 1/(3.7755 K + 0.1887)$	( $r = 0.99$ )
Hailwood-Horrobin model:	$a_{w(p=s)} = 1/(2.7070 K - 0.3489)$	( $r = 0.93$ )

The greater the multilayer energy constant  $K$  was, the lower the level at which primary sorption was equal to secondary sorption. The results of the GAB isotherm led to values that were less than half of the water activities given by the Dent model; nevertheless, both models showed the same relationship between water activity and  $K$ . The mean values of  $K$  for absorption and desorption were 0.831 and



**Figure 7.** Relationship between monolayer size and regain where primary and secondary sorption are equal.

0.777 respectively. No significant effect of delignification or, obviously, delignification time on both the multilayer constant and water activities in desorption was observed. The mean water activities that resulted in equal primary and secondary moisture uptake during absorption and desorption were 0.310 and 0.320 for the GAB model, 0.602 and 0.643 for the Dent model and 0.525 and 0.571 for the Hailwood-Horrobin model, respectively.

#### 4.5.5. Regain values at which primary moisture uptake is equal to secondary moisture uptake

Estimations of regain using the three models led to different results. The highest values are those given by the Dent model, which is closely followed by the Hailwood-Horrobin model, and the lowest values are those given by the GAB model, which were greater than 50% of the results given by the first two abovementioned models.

A very strong relationship was observed between these values and the size of the monolayer,  $X_m$ , estimated by both the GAB and Dent models. Figure 7 shows the relationship between the size of the monolayer,  $X_m$ , and the values at which the primary regain values were equal to the secondary values according to the three different models.

The regain values at which primary sorption was equal to secondary sorption according to the Dent and Hailwood-Horrobin models,  $X_{(p=s)}$ , were higher than those given by the GAB model because the inflection point of the isotherm,  $X_{(inf)}$ , was higher than that of the Dent model. The best correlations with the size of the monolayer were as follows:

Dent model:	$X_{(p=s)} = \text{EXP} (1.0338 + 0.2324 X_m)$	$(r = 0.999)$
HH model:	$X_{(p=s)} = \text{EXP} (0.8320 + 0.2468 X_m)$	$(r = 0.999)$
GAB model:	$X_{(inf)} = \text{EXP} (0.4044 + 0.2433 X_m)$	$(r = 0.999)$

The greater the size of the monolayer  $X_m$  was, the higher the regain at which primary sorption was equal to secondary sorption. The original sample measured in desorption

exhibit the highest  $X_m$  and  $X_{(p=s)}/X_{(inf)}$  values. In contrast, the lowest values of  $X_m$  and  $X_{(p=s)}/X_{(inf)}$  were obtained for the delignified samples during absorption. The  $X_m$  and  $X_{(p=s)}/X_{(inf)}$  of the original sample measured during absorption and those of the delignified samples measured during desorption showed very similar results between the two extremes. The delignification time did not significantly affect the results.

## 5. Conclusions

As regarding the way to measure the influence of the time of the alkaline delignification on the moisture uptake behaviour of hemp, to evaluate their ability to be used in the production of next-to-skin goods (garments, household textiles and medical devices), the following conclusions have been reached:

1. Remaining lignin after delignification, plays a determinant role in moisture uptake at low water activities, while cellulose plays this role at high water activities. The sorption ratio of hemp delignified for 2 hours is 0.769, while those delignified for 3 and 4 hours slightly decreases the sorption ratio to near 0.755, with no significant differences between them.
2. Delignification reduces hysteresis at water activities lower than 0.4, while at higher water activities, the opposite occurs. Lignin favours water uptake but hinders accessibility to cellulose, resulting in a weaker linkage of water, which decreases hysteresis at higher water activities. Hysteresis of sample delignified for 2 hours was closer to the original hemp, than the samples delignified for 3 and 4 hours, which were not different between them.
3. The parameters derived from the three different models fitted to the absorption/desorption isotherms, enable to conclude the following:
  - a. Lignin greatly contributes to the size of the monolayer. The size of the monolayer measured in desorption is always greater than that measured in absorption, where differences between delignified samples are amplified. The shorter the time of delignification, the greater the size of the monolayer.
  - b. The energy constants of the monolayer are greatly affected by lignin, which causes great differences between absorption and desorption. Raw hemp shows the highest differences, while those of delignified samples were shorter and closer to those of the original sample measured in absorption. The greater the time of delignification, the lower the monolayer energy constant of delignified hemp.
  - c. The energy constant of the multilayer shows a greater range of variation in delignified samples than in the original sample. Results in absorption were higher than those in desorption regardless the time of delignification.

- d. The level of water activity at which secondary water scores the primary one decreases with the energy constant of the multilayer, so the greater the constant is, the lower the water activity at which primary equal to secondary one.
  - e. The level of regain at which primary and secondary water are the same is strongly related and grows with the size of the monolayer.
  - f. Estimations in desorption show best fits, consequently it seems to be better the use of isotherms in desorption to analyse the effect of delignification time on the size of the monolayer, energy constants and levels of water activity and regain where secondary water scores the primary one.
4. The moisture uptake of delignified hemp with lignin content lower than 3% shows a moisture uptake behaviour close to that of cotton at higher relative humidities where cellulose plays the most important role.

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## ORCID

Albert M. Manich  <http://orcid.org/0000-0002-9835-2850>  
 Manuel J. Lis Arias  <http://orcid.org/0000-0002-2026-085X>  
 Sonia Pérez-Rentero  <http://orcid.org/0000-0002-7732-4543>  
 Marta Riba-Moliner  <http://orcid.org/0000-0003-0001-2055>  
 Gabriela Mijas  <http://orcid.org/0000-0002-4688-7175>  
 Meritxell Martí  <http://orcid.org/0000-0001-9681-6466>  
 Diana Cayuela  <http://orcid.org/0000-0002-1048-8340>

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