

## ARTICLE

# Influence of alkaline delignification on moisture uptake behavior and bonding enthalpies of hemp

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## Abstract

Raw hemp fibers are alkaline delignified to evaluate the effect of lignin on the moisture uptake behavior of hemp. Samples are subjected to moisture absorption/desorption isotherms from 5% to 95% relative humidity at three different temperatures (15, 25, and 35°C). The sorption ratio between delignified and untreated hemp is lowered by 25%. Hysteresis makes evident the greater influence of lignin on moisture binding at low relative humidity while at high relative humidity, cellulose plays the most important role. The GAB, Hailwood-Horrobin and Dent models are fitted to absorption/desorption isotherms. Delignification and temperature decrease the size of the monolayer. The energy constants of the monolayer differ according to the model used. Lignin causes great differences between absorption and desorption. The greater the temperature is, the lower the monolayer energy constant. The energy constants of the multilayer are identical for the three models, showing a greater range of variation in delignified samples than in the untreated samples. Based on primary and secondary energy constants, bonding enthalpies are determined. Estimations in desorption show higher correlation coefficients with the energy constants, which enables to conclude that measures in desorption better explain the effect of delignification on the water uptake behavior of hemp.

## KEYWORDS

adsorption, biopolymers and renewable polymers, cellulose and other wood products

## 1 | INTRODUCTION

Hemp (*Cannabis sativa* L.), is a plant of the Cannabaceae family that has been grown and utilized in a variety of environments and countries worldwide.<sup>1,2,3</sup> The ability of hemp to root deeply makes it a low nitrogen- and irrigation-demanding crop, yielding significant

environmental benefits compared to other competing fiber-producing crops, such as cotton. Hemp is able to grow in areas contaminated with heavy metals, favoring bioremediation.<sup>4,5,6</sup>

Hemp fibers can be considered a network of ultrafine cellulose fibrils embedded in a matrix of hemicelluloses and lignin.<sup>7</sup> Lignin in bast fibers makes them stiff and

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hinders their breakdown and spinnability.<sup>8</sup> The main objective of delignification is to separate fiber bundles into elementary fibers by removing lignin that holds bundles together, enabling the elementary "cottonized" fibers to be spun using the conventional cotton spinning process.

The composition and delignification process of hemp have been widely described.<sup>9</sup> The comparison between different cottonization processes for a wide range of bast fibers, including hemp, has been studied, although many works have focused on flax.<sup>10</sup>

Cottonization of hemp, as that of the other bast fibers, has been approached from mechanical, chemical and enzymatic points of view in combination with wet vapor application processes. Cottonization modifies the fiber structure, increasing the specific surface area and causing changes in crystallinity, thermal stability, mechanical properties and moisture absorption and desorption behavior.<sup>11,12,13</sup> The predominant task in preparing hemp fibers for further processing is to remove the non-cellulosic components, improving sorption and other fiber properties without damaging the cellulose of the fiber.<sup>14</sup> Attempts to explain the individual roles of hemicelluloses and lignin removal in the moisture uptake behavior of chemically modified hemp fibers have been made.<sup>7</sup> These modifications favor the application of bast fibers alone or in blends to the manufacture of substrates focused on the production of clothing and home textiles.

Moisture sorption breaks secondary interactions between macromolecules of cellulose by water molecules absorbing into the fibers by hydrogen bonds, causing swelling. Lignin may contribute to moisture sorption via its carboxyl and both aliphatic and phenolic hydroxyl groups.<sup>15</sup> The effect of lignin on sorption and hygroexpansion has been frequently discussed, and it is agreed that the more hydrophilic cellulose and hemicelluloses in the cell wall being surrounded by the less hydrophilic lignin is essential for the relationship between water and cell wall components.

Lignin can be considered an easily accessible moisture-absorbing material, the removal of which causes significant alterations to the fiber surface and accessibility.<sup>16</sup> Delignification modifies the moisture behavior of fibers because of changes caused in chemical composition, crystallinity and pore structure.<sup>7</sup>

## 1.1 | Characterization of moisture uptake behavior during absorption and desorption

The moisture uptake held within a cellulose fiber exerts a profound influence on its rheological properties. The water uptake versus the bone-dry mass of a sample is

known as "regain". The relation between regain from very low to very high levels of relative humidity of the surrounding air at constant temperature are measured to generate the sorption isotherm.

Rheological tests are frequently performed under controlled conditions of relative humidity and temperature; consequently, it is useful to know the sorption isotherm for a particular material being investigated, as the variation in the rheological property with moisture regain may be calculated from its variation with humidity. Simple relationships may be expected between moisture regain and rheological behavior since it is the amount of water within the fiber that governs its behavior.

### 1.1.1 | The sorption ratio

Meredith<sup>17</sup> found that the regain of viscose compared with that of cotton at the same relative humidity from 5% to 85% RH results in an almost constant number that he called the "sorption ratio". By means of this number, he found that, provided the isotherms of cotton were known, it was possible to express the regain of another fiber with fair accuracy. This was based on the assumption that the nature of absorption in different cellulosic fibers was similar and differed only in quantity.

The sorption ratio enables us to determine the effect caused by different treatments on fiber regain. To characterize fibers, Meredith uses the mean value of the sorption ratio determined during absorption and desorption when subjected to a wide range of relative humidity.

### 1.1.2 | Temperature and regain

Weigerink<sup>18</sup> investigated the effect of temperature on the regain of cellulosic fibers at different relative humidity levels. He found that in a wide range of temperatures from 20 to 100°C, the regain  $X$  decreased linearly with the increase in the reciprocal of the absolute temperature  $T$  according to the following relationship:  $\text{Log } X = A - B \cdot (1/T)$ . He found that slope  $B$  differed between different cellulosic fibers and was able to explain the effect of temperature on regain at different levels of relative humidity.

### 1.1.3 | Hysteresis

The desorption isotherm of a hygroscopic material such as cellulosic fibers lies above the absorption isotherm because the amount of water held at a given relative humidity is greater in fibers coming from higher humidity than those from lower humidity.

Moisture in fibers, in addition to modifying the intrinsic properties of fibers, causes anisotropic swelling that alters the geometry of the fiber. In cellulosic fibers, the molecules show a preferred orientation in the direction of the fiber axis, and the crystallites are much longer than they are wide. The same thickness of the non-crystalline fiber-water phase surrounding a crystalline region will produce greater swelling laterally than longitudinally. Changes in length and diameter with relative humidity show hysteresis, similar to that of moisture regain.<sup>17</sup>

Hysteresis can be measured at different relative humidity levels by the growth in regain measured in desorption  $X_d$  versus that in absorption  $X_a$  as a percentage, according to the following relationship:  $H (\%) = 100 (X_d - X_a) / X_a$ .<sup>19</sup>

## 1.2 | Modeling the absorption-desorption isotherms

The classic Brunauer, Emmett and Teller (BET) absorption model is based on the good correlation between the number of water molecules linked to the first absorption layer and the number of polar groups of the absorbent. This process is known as "primary absorption". It is assumed that each polar group links one water molecule, which, in turn, can capture other molecules diffusing to the interior of the material thanks to the increase in relative humidity of the environment, giving rise to "secondary absorption".

The BET equation is used to calculate the size of the monolayer of the most diverse materials and is recognized by the IUPAC for the calculation of the specific surface of absorption. In 1985, the Colloid and Surface Chemistry Commission recommended the BET equation to estimate the size of the monolayer at relative humidity RH between 5% and 30%. The relative humidity RH (%) can also be identified as the water activity  $a_w$  (RH/100), which corresponds to the molar fraction of moisture versus the moisture concentration at saturation. If the relative humidity ranges from 0% to 100%,  $a_w$  will vary from 0 to 1. Moisture uptake of sample  $X$  will be measured as "regain" (bone-dry weight in %), and the models fit the evolution of regain as a function of water activity  $a_w$ .

### 1.2.1 | GAB model

The Guggenheim, Anderson and de Boer (GAB) model estimates the size of the monolayer in a range of  $a_w$  from 0.05 to 0.8–0.9,<sup>20</sup> which enables the estimation of the primary and secondary absorption. BET and GAB isotherms are based on the same hypothesis and share the size of the monolayer  $X_m$  and its energy constant  $C$ . Additionally, the GAB model estimates the multilayer

energy constant  $K$ , and both  $C$  and  $K$  describe the plot shape of the sample regain  $X$  versus water activity  $a_w$ .

$C$  defines the initial convexity at low water activities, proportional to the variation in ratio between absorption and desorption rates, when the partial pressure of humidity for the monolayer is modified.  $K$  defines the concave shape at greater water activities and depends on the ratio between the absorption and desorption rates of the water molecules placed in the upper layers. The lower the  $K$  is, the less structured the multilayer sorbate is in relation to the pure liquid state.  $K$  grows with the interaction between sorbate and sorbent.<sup>20</sup>

According to various authors,<sup>21</sup> the level of water activity at which secondary absorption begins to overcome the primary absorption is determined by the minimum of the isotherm derivative, which corresponds to its inflection point [ $a_{w(\text{inf})}$ ,  $X_{(\text{inf})}$ ].

### 1.2.2 | Hailwood-Horrobin model

The Hailwood-Horrobin model<sup>22</sup> splits the absorption isotherm between primary absorption on the monolayer and secondary absorption on the multilayers. Primary absorption measures the hydrated polymer P—H<sub>2</sub>O caused by the reaction between the free water dissolved into the polymer H<sub>2</sub>O<sub>sol</sub> and the dry polymer P forming a single solid phase with the three components in equilibrium.  $K_1$ , the equilibrium constant between the hydrated polymer and its components (dry polymer and free water dissolved into the polymer), is the monolayer constant. Secondary absorption depends on the equilibrium between the water vapor in the surrounding atmosphere and water dissolved into the polymer. The equilibrium constant  $K$  relates the concentration of moisture measured as the water activity from  $a_w$  and the water dissolved into the polymer H<sub>2</sub>O<sub>sol</sub>.

If the amount of water absorbed is referred to as the molecular weight of polymer  $M$  (g mol<sup>-1</sup>), moisture uptake can be split between moles of water dissolved into the polymer and moles of water linked to the polymer. Consequently, the sample regain  $X$  (%) can be expressed as the sum of bound water in the monolayer (primary water)  $X_p$  and free water in the multilayer (secondary water)  $X_s$ . The whole regain  $X$  will result from the addition of  $X_p = (1800 / M) [K_1 K a_w / (1 - K_1 K a_w)]$  and  $X_s = (1800 / M) [K a_w / (1 - K a_w)]$ .

The water activity at which the primary water ties with the secondary water  $a_{w(p=s)}$  and the regain at this point  $X_{p=s}$  can be determined. Primary and secondary water determined by the Hailwood-Horrobin model are equivalent to those given by the GAB model.<sup>23</sup>

$M$  is always greater than the molecular mass of a polar group in the fiber. This can be justified by the presence of

crystalline areas inaccessible to water that are considered the molecular mass of the accessible polar group. It also estimates the mass of material inaccessible to water.

### 1.2.3 | The Dent model

The Dent model,<sup>24</sup> as the Hailwood-Horrobin model, considers the evolution of primary  $X_p$  and secondary  $X_s$  absorption as a function of water activity  $a_w$ , where  $X$  is the whole regain, and the addition of the two components results in  $X = X_m b_o a_w / [(1 - b a_w) (1 - b a_w + b_o a_w)]$ , where  $X_m$  is the size of the monolayer as that of the GAB model,  $b_o$  is the energy constant of the primary absorption, and  $b$  is the energy constant of the secondary absorption. The two components are split as follows:  $X_p = X_m b_o a_w / [1 + (b_o - b) a_w]$  and  $X_s = X_m b_o b a_w^2 / [1 + (b_o - b) a_w] / (1 - b a_w)$ . As in the Hailwood-Horrobin model, the water activity at which the primary absorption equals the secondary absorption  $a_{w(p=s)}$ , and the regain at this point  $X_{p=s}$  can also be determined.

### 1.3 | Enthalpies of primary (monolayer) and secondary (multilayer) bonding

According to Kapsalis,<sup>25</sup> the slope of the linear fitting between the logarithm of the primary and secondary energy constants given by the GAB model, as a function of the inverse of the absolute temperature  $T$ , is related to the variation in enthalpy caused by the primary and secondary moisture uptake:

$$\text{Primary absorption: } \log C = \log \gamma + (Hm - Hn)/(R T) \quad (1)$$

$$\text{Secondary absorption: } \log K = \log \delta + (Hp - Hn)/(R T) \quad (2)$$

where  $\gamma$  and  $\delta$  are entropic factors,  $Hm$  is the enthalpy of water molecules linked to the monolayer,  $Hn$  is that of the water linked to the multilayer, and  $Hp$  is the enthalpy of the free water.  $R$  is the gas constant  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  or  $0.4619 \text{ J K}^{-1} \text{ g}^{-1}$  if water is measured in grams instead of mols.

### 1.4 | Objectives

The objective of this work was to study the effect of the alkaline delignification of hemp on its moisture uptake through the evaluation of the sorption ratio, the effect of

temperature on regain during absorption and desorption, and the hysteresis of the isotherms; by fitting the different models to the isotherms, estimations of the monolayer size were determined during both absorption and desorption, and the energy constants of primary and secondary sorption, the moisture uptake at saturation, the levels of water activity and regain at which primary absorption equals secondary absorption and, finally, the primary and secondary bonding enthalpies were determined.

### 1.5 | Novelty and justification of the work

The work has been done under the project "Preparation and functionalization of hemp for textile substrates" to study one of its objectives: the application of hemp replacing cotton in clothing, household textiles and medical devices, in order to reduce their fabrication on cotton import. The characterization of the moisture uptake behavior is very important to evaluate the adequacy of goods in contact with human body as occurs in clothing and medical devices.

The novelty of the paper lies on the application of three tools that easily characterize the moisture uptake behavior, that can be extended to other lignocellulosic fibers:

- The sorption ratio defined by Meredith<sup>17</sup> more than 60 years ago, that helps to easily characterize this behavior.
- The combination of hysteresis and sorption ration, that enables to identify the levels of humidity where lignin or cellulose play the most influencing role on moisture binding.
- The calculation of the enthalpies of primary and secondary bonding normally based on GAB model but, in this work, extended to Hailwood-Horrobin and Dent models of sorption isotherm, that enable to characterize the bonding energy of water to lignin and cellulose.

Additional novelties are based on the evaluation of the contribution of lignin on the size of the monolayer, its effect on the different behavior between absorption and desorption of moisture, and to confirm that the desorption isotherm is the most adequate to characterize the effect of delignification on the moisture uptake behavior of the fiber.

## 2 | MATERIALS

### 2.1 | Untreated hemp

Raw hemp fibers were supplied by CELESA, and after being rinsed in distilled water at room temperature for

10 min to remove impurities, dust, and water-soluble salts, the hemp was used as untreated raw material.

## 2.2 | Delignified hemp

The untreated hemp fibers were subjected to an alkaline delignification treatment under the following conditions: NaOH, 40 g L<sup>-1</sup>; surfactant Hostapal DTC, 1.5 g L<sup>-1</sup>; temperature, 110°C; time, 3 h; and water bath ratio, 1:20. The samples were then rinsed with distilled water at 80°C and subjected to a neutralization treatment with acetic acid and two final rinses with distilled water. After drying, delignified hemp was obtained.

## 3 | METHODS

### 3.1 | Lignin content

The lignin content was chemically determined following the TAPI T222 om-15 standard. The results were correlated with those obtained by thermogravimetric analysis (TGA), and the lignin content in % was determined according to procedures described elsewhere.<sup>9</sup>

### 3.2 | Moisture absorption/desorption trials

Moisture absorption/desorption isotherms were performed at three temperatures (15, 25, and 35°C) on samples of approximately 10 mg using the Q5000SA dynamic vapor sorption DVS analyzer (TA Instruments) according to the following procedure:

1. Initial drying was conducted at 60°C and 0% relative humidity for 300 min.
2. Pre-stabilization was performed at 0% relative humidity at the isotherm temperature, and then a relative humidity RH of 5% until stabilization.
3. *Absorption process*: Samples stabilized at 5% RH were subjected to increasing absorption stages to stabilization from 15% to 25%, 35%, 45%, 55%, 65%, 75%, 85%, and 95% RH.
4. *Desorption process*: The samples stabilized at 95% RH were subjected to decreasing desorption stages to 85%, 75%, 65%, 55%, 45%, 35%, 25%, 15%, and 5% RH to complete a cycle of moisture absorption/desorption.
5. The maximum time that the samples remained at each absorption/desorption stage was 500 min. The time could be shortened if quasi-stabilization conditions were reached (variation in sample mass lower

than 0.01% for 18 min). If this condition occurred, the sample proceed 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 and raw hemp at different water activities  $a_w$  from 0.05 to 0.85 was determined during absorption and desorption at the three different temperatures according to the procedure described in section 1.1.1. The effect of measuring conditions (absorption/desorption, water activity, and temperature) on the sorption ratio between delignified and untreated hemp was determined by analysis of variance.<sup>26</sup>

### 3.4 | Temperature and regain

Regain values at the same water activity level measured on the isotherms at 15, 25, and 35°C enabled the determination of the effect of temperature on moisture regain by fitting a linear regression between regain  $X$  and temperature  $T$ , according to the model  $X = A - B \cdot T$ , where  $A$  is the initial constant that predicts regain at 0°C (%) and  $B$  is the slope that can be considered as the "thermal regain loss", that is, the decrease in regain caused by the increase of temperature in tens of degrees (%/10°C).

Values of  $A$  enabled plotting the predicted isotherms of both the untreated and delignified hemp samples at 0°C. Linear regression was performed with the modified Weigerink model<sup>18</sup> explained in section 1.1.2, disregarding the logarithmic transformation of regain and considering a linear relationship with temperature in degrees centigrade instead of the reciprocal of the absolute temperature.

### 3.5 | Hysteresis

As explained in section 1.1.3, hysteresis was measured at different levels of water activity from 0.05 to 0.85 according to the relationship  $H (\%) = 100 (X_d - X_a) / X_a$ , where  $X_d$  is the regain of the sample measured in desorption and  $X_a$  is the regain of the sample measured in sorption.

### 3.6 | Fitting the isotherms of moisture absorption/desorption

The software of the DVS analyzer automatically gave the parameters of the GAB absorption isotherm,<sup>27</sup> which were used as initial estimators for obtaining the parameters of the absorption and desorption isotherms by the application

of an iterative non-linear regression procedure described elsewhere.<sup>28</sup> This procedure allowed for prediction of the moisture uptake  $XI$  at saturation  $a_w = 1$ , which was used for the estimation of the desorption isotherm together with regain values during desorption from  $a_w = 0.85$  to  $a_w = 0.05$ . The application of the non-linear regression procedure using the initial estimators given by the absorption model enabled fitting the GAB model during desorption.

Initial estimators of the two other fitted isotherms during absorption were obtained following the procedures described for the Hailwood-Horrobin<sup>22</sup> and Dent<sup>24</sup> models.

**TABLE 1** Summary of BET, GAB, Dent, and Hailwood-Horrobin isotherms of absorption/desorption and parameters

Model	Mathematical equation
BET <sup>29</sup>	$X = X_m C a_w / [(1 - a_w)(1 - a_w + C a_w)]$
GAB <sup>27</sup>	$X = X_m C K a_w / [(1 - K a_w)(1 - K a_w + C K a_w)]$
Dent <sup>24</sup>	$X = X_m b_0 a_w / [(1 - b a_w)(1 - b a_w + b_0 a_w)]$
H-H <sup>22</sup>	$X = (1800/M) [K_1 K a_w / (1 - K_1 K a_w) + K a_w / (1 - K a_w)]$
Parameter	Definition
<u>Variable</u> :	Water activity expressed as relative moisture pressure or molar fraction.
$a_w$	
<u>Response</u> :	Moisture uptake of the sample measured as regain (g of water / 100 g of bone-dry sample).
$X$	
<u>Primary absorption</u> :	Size of the monolayer as g of bonded water / 100 g of dry sample.
$X_m$	
$M$	Molecular mass of the monohydrated sample (g mol <sup>-1</sup> )
$C$	
$b_0$	Monolayer energy constant of the GAB model (*)
$K_1$	
<u>Secondary absorption</u> :	Monolayer energy constant of the Dent model.
$K$	
$b$	Monolayer energy constant of the Hailwood-Horrobin model.
	<i>These constants are related to the difference between the free enthalpy of water in the liquid state and in the monolayer. They are proportional to the relationship between the rates of absorption and desorption of water molecules at the monolayer.</i>
	(*) $C = \gamma \cdot \exp[(Hm - Hn)/(R \cdot T)]$ (Equation 1)
	Multilayer energy constant of GAB (**) and Hailwood-Horrobin models.
	Multilayer energy constant of the Dent model.
	<i>The constants are related to the relationship between the absorption and desorption of water molecules at the multilayer. These constants coincide with the equilibrium constant between the external water vapor molecules and those absorbed in the multilayer.</i>
	(**) $K = \delta \cdot \exp[(Hp - Hn)/(R \cdot T)]$ (Equation 2)

The application of the same iterative non-linear regression procedure enabled fitting the models during absorption that, as was conducted for the GAB model, gave prediction of the maximum regain  $XI$  at  $a_w = 1$ , which together with the results given by the desorption isotherm from  $a_w = 0.85$  to  $a_w = 0.05$ , allowed the calculation of the Hailwood-Horrobin and Dent models during desorption.

The goodness of fit of all models during absorption and desorption at different temperatures (15, 25, and 35°C) were estimated by the determination coefficient  $R^2_{adj}$  adjusted to the degrees of freedom.

### 3.7 | Enthalpies of primary and secondary absorption

According to the equations of Kapsalis described in 1.3 that use the energy constants given by the GAB model, the slopes  $(Hm - Hn)/R$  and  $(Hp - Hn)/R$  enable the determination of the variation in enthalpy caused by the primary absorption  $\Delta H_p (= Hm - Hn)$  when water molecules move from the multilayer to the monolayer and that caused by the secondary absorption  $\Delta H_s (= Hp - Hn)$  when free water molecules join the multilayer.

Estimations of enthalpy were conducted with the absorption and desorption isotherms, and the primary and secondary energy constants given by the Hailwood-Horrobin and Dent models were also used, and the results were compared with those given by the GAB model.

Table 1 summarizes the different models of the absorption/desorption isotherms, the meaning of the parameters and their relations with the enthalpies of primary and secondary absorption.

## 4 | RESULTS AND DISCUSSION

### 4.1 | Lignin content

The lignin contents were 6.2% for the untreated raw hemp and 2.9% for the alkaline delignified hemp, the treatment process of which removed 53.2% of the lignin.

### 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 from 0.05 to 0.95 water activity and from 0.85 to 0.05 water activity during desorption for the raw hemp (OR) and alkaline delignified hemp (3 U), respectively, in the isotherms at the three different temperatures (15, 25, and 35°C).

### 4.3 | Sorption ratio

Based on the experimental results of Table 2, the sorption ratio between the delignified hemp and the untreated hemp was determined according to temperature, water activity at which the samples were stabilized from 0.05 to 0.85 and the method of stabilization (absorption or desorption). Table S1 of the Supporting Information shows the results.

The application of analysis of variance using standard statistical software<sup>30</sup> to the results allowed for evaluating the effect temperature, water activity and method of stabilization (absorption/desorption) on this parameter. Temperature of the isotherm had no significant effect on the sorption ratio. The mean the sorption ratio was approximately 0.75, which means that delignification caused a decrease of 25% in the moisture uptake of hemp. Water activity and the method of stabilization (absorption/desorption) showed a very significant interaction and affected the sorption ratio, as shown in Figure 1.

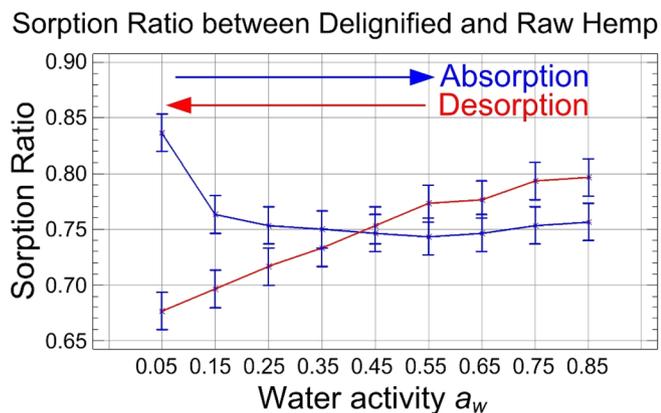
Moisture absorption begins with dry fibers, and although the delignification treatment reduced lignin by

more than 50%, the remaining lignin played a significant role in absorbing free moisture from the environment at low water activities, starting with a high sorption ratio (0.84) that decreased with increasing water activity. When  $a_w$  exceeded 0.25, the sorption ratio remained at approximately 0.75, which can be attributed to the role of 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 fiber, which altered the accessibility of energetically polar sites.<sup>31</sup> Moisture sorption and desorption is a 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 migrate to the environment, being progressively followed by the more internal secondary sorbed molecules that progressively decreased<sup>32</sup> as moisture was removed. The sorption ratio

**TABLE 2** Regain  $X$  of the samples of the untreated (OR) and the delignified hemp (3 U) when the stabilization conditions were reached in % on dry mass, when subjected to a cycle of absorption/desorption according to the different levels of the water activity  $a_w$  at the three temperatures of the isotherms (15, 25, and 35°C)

Sample ref. and temp.	OR 15°C	OR 25°C	OR 35°C	3 U 15°C	3 U 25°C	3 U 35°C
$a_w$ levels in absorption:						
0.05	1.110	1.110	1.001	0.9843	0.8973	0.8127
0.15	2.986	2.832	2.581	2.307	2.146	1.971
0.25	4.535	4.179	3.829	3.399	3.128	2.903
0.35	5.863	5.415	4.977	4.393	4.018	3.758
0.45	7.200	6.642	6.132	5.378	4.898	4.625
0.55	8.646	8.013	7.420	6.458	5.869	5.567
0.65	10.41	9.569	8.847	7.765	7.067	6.669
0.75	12.79	11.65	10.77	9.563	8.694	8.137
0.85	16.36	14.85	13.55	12.39	11.15	10.26
0.95	24.79	21.43	18.84	19.29	16.50	14.34
$a_w$ levels in desorption:						
0.85	18.68	16.40	14.69	14.83	13.13	11.72
0.75	14.98	13.36	12.06	11.86	10.65	9.554
0.65	12.50	11.24	10.33	9.806	8.816	7.990
0.55	10.69	9.699	8.631	8.224	7.426	6.705
0.45	9.182	8.282	7.395	6.852	6.179	5.588
0.35	7.747	6.929	6.160	5.638	5.076	4.569
0.25	6.281	5.593	4.904	4.451	4.010	3.544
0.15	4.661	4.077	3.513	3.175	2.843	2.501
0.05	2.599	2.085	1.658	1.677	1.458	1.132



**FIGURE 1** Mean values of sorption ratio at 15, 25, and 35°C including confidence intervals at 95% between delignified and raw hemp as a function of the water activity and the method of stabilization (absorption/desorption) [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

during desorption progressively decreased with the reduction in water activity. Whole means showed that delignification decreased the sorption ratio of hemp by 75.4% (76.1% in absorption and 74.6% in desorption).

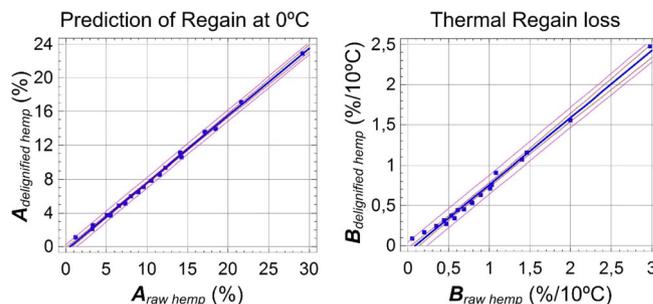
#### 4.4 | Temperature and regain

Using the results of Table 2, linear regressions between regain  $X$  and temperature  $T$  at different levels of water activity according to the method of stabilization (absorption/desorption) for the raw and delignified hemp were constructed by fitting the model  $X = A - B \cdot T$ , where  $A$  is the initial constant that predicts the regain at 0°C in % and  $B$  is the slope that estimates the thermal regain loss in %/10°C. Table S2 and Figures S1 and S2 of the Supporting Information show the strong relationship between the initial constant  $A$  and the slope  $B$  according to the sample and the method of stabilization (absorption/desorption).

The effect of delignification on the influence of temperature on regain can be measured by the linear regression between the results yielded by delignified hemp vs raw hemp for the parameters  $A$ , the estimated regain at 0°C, and  $B$ , the thermal regain loss. The results plotted in Figure 2 are the following:

1. Estimated regain at 0°C:  $A_{delig.} = -0.4094 + 0.7965 \cdot A_{raw}$ ,  $r = 0.999$
2. Thermal regain loss:  $B_{delig.} = -0.0733 + 0.8317 \cdot B_{raw}$ ,  $r = 0.996$

The slopes of the linear regressions show that the 44% reduction in the lignin content decreased both the



**FIGURE 2** Plot of the linear regressions between the predicted regain at 0°C and the thermal regain loss of delignified hemp versus raw hemp to estimate the effect of delignification on the influence of temperature on regain [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

estimated regain at 0°C and the thermal regain loss by approximately 20% and 17%, respectively. Delignification decreased the influence of temperature on the moisture uptake of hemp. The Supporting Information shows in Figure S2 the closer position between the absorption and desorption fits of the delignified sample than that of the fits of the raw hemp.

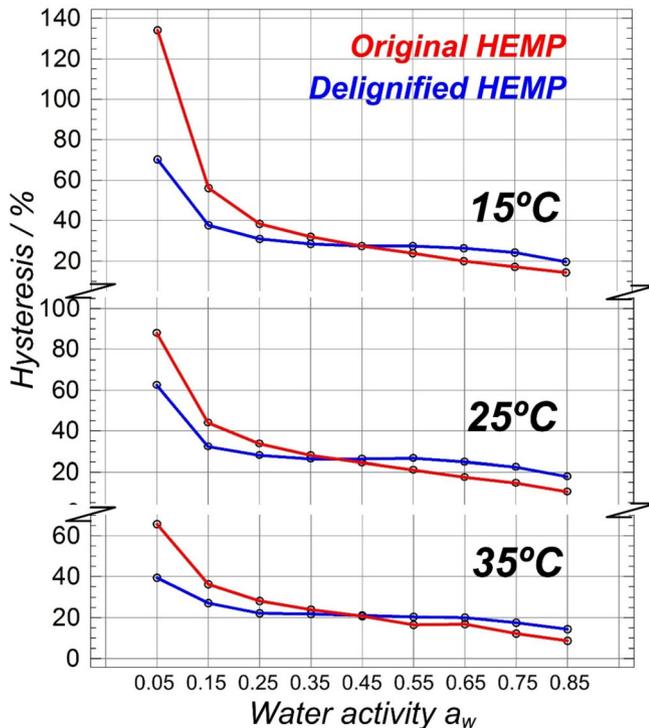
#### 4.5 | Hysteresis

The application of the equation given in section 3.5 to the results in Table 2 enabled determination of the hysteresis by comparing regain in desorption vs. that in absorption from 0.05 to 0.85 water activity for the untreated and delignified hemp at the three temperatures of the isotherms. Table S3 of the Supporting Information shows the results.

The analysis of the results was performed by the application of analysis of variance to evaluate the effect of delignification on this parameter. Delignification decreased hysteresis at water activities lower than 0.45, while at higher values, hysteresis of the delignified hemp remained above that of the untreated hemp. Hysteresis was also greatly influenced by water activity, where the highest hysteresis values were observed at the lowest values of water activity, which was related to molecules of water directly linked to the polymer. As the water activity increased, hysteresis gradually decreased, reaching the lowest values at the highest water activity. The temperature of the isotherm also affected hysteresis: the greater the temperature was, the lower the hysteresis. Figure 3 shows the results according to water activity and temperature.

Hysteresis seems to be due to hydroxyl groups taking part in absorption and desorption, which are modified by swelling caused by water uptake, which also modified the

physical state and properties of the fiber. Delignification reduced hysteresis, probably because of the loss of free hydroxyl groups of wood that fix water by hydrogen bonds.<sup>15</sup> Figure 3 suggests that lignin could play a prominent role in hysteresis at low water activities, while cellulose played a strong role at high water activities.



**FIGURE 3** Hysteresis of the untreated and delignified hemp as a function of water activity and temperature of the isotherm [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**TABLE 3** GAB model. Parameters of the absorption and desorption isotherms as a function of the sample and temperature of the isotherm: Monolayer size  $X_m$ , energy constants of the monolayer  $C$  and the multilayer  $K$ , determination coefficient of the model  $R^2_{adj}$ , regain at saturation  $X_I$  (% 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	$R^2_{adj}$ /%	$X_I$ /%	$a_{w(inf)}$	$X_{(inf)}$ /%
<i>Absorption isotherm :</i>							
OR 15°C	5.09	8.61	0.840	99.77	31.21	0.297	5.032
OR 25°C	4.91	8.20	0.818	99.86	26.20	0.305	4.786
OR 35°C	4.81	7.21	0.794	99.91	22.50	0.313	4.507
3 U 15°C	3.64	10.05	0.856	99.77	24.94	0.292	3.738
3 U 25°C	3.49	9.21	0.834	99.87	20.63	0.300	3.512
3 U 35°C	3.57	7.59	0.800	99.93	17.23	0.311	3.396
<i>Desorption isotherm :</i>							
OR 15°C	6.29	16.19	0.801	99.89	31.21	0.301	6.936
OR 25°C	5.93	13.33	0.777	99.87	26.20	0.316	6.389
OR 35°C	5.68	10.35	0.754	99.91	22.50	0.331	5.863
3 U 15°C	5.03	10.39	0.803	99.93	24.94	0.311	5.197
3 U 25°C	4.83	8.99	0.773	99.96	20.63	0.323	4.824
3 U 35°C	4.78	7.12	0.736	99.99	17.23	0.337	4.458

## 4.6 | Fitting the isotherms of absorption/desorption

The different models of absorption/desorption were fitted to the results in Table 2 using the procedures described in section 3.6, and Tables 3, 4 and 5 show the results of GAB, Hailwood-Horrobin and Dent model fitting, respectively, all of which yielded 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 the primary and secondary absorption reach the same level.

Regression analysis between the estimators given by the three models allowed for identification of the relationship between these parameters, and the parameters were grouped based on the significance of their relationships.

### 4.6.1 | Monolayer size

The estimation of the size of the monolayer through the GAB and Dent models led to the same results. The relationship between the size of the monolayer  $X_m$  measured in g of water bonded to 100 g of the sample and that measured by the molecular mass  $M$  of the monohydrated sample given by the Hailwood-Horrobin are linked through the Equation  $M = 0.3878 + 1797.91/X_m$  with a correlation coefficient  $r = 1.00$ , which is shown in Figure 4.

The size of the monolayer measured during desorption was always higher than the results given when measured during absorption. Lignin greatly contributed to

Reference	$M/\text{g mol}^{-1}$	$K_1$	$K$	$X_1/\%$	$R^2_{adj}/\%$	$a_{w(p=s)}$	$X_{(p=s)}/\%$
<i>Absorption isotherm :</i>							
OR 15°C	353.3	7.61	0.840	31.21	99.77	0.517	7.822
OR 25°C	366.6	7.20	0.818	26.20	99.86	0.527	7.427
OR 35°C	374.3	6.21	0.794	22.50	99.91	0.529	6.949
3 U 15°C	493.7	9.05	0.856	24.94	99.77	0.519	5.841
3 U 25°C	515.9	8.21	0.834	20.63	99.87	0.526	5.463
3 U 35°C	504.7	6.59	0.800	17.23	99.93	0.530	5.254
<i>Desorption isotherm :</i>							
OR 15°C	286.3	15.19	0.801	31.21	99.89	0.583	11.023
OR 25°C	303.5	12.32	0.777	26.20	99.87	0.591	10.081
OR 35°C	317.0	9.35	0.754	22.50	99.91	0.592	9.161
3 U 15°C	358.0	9.39	0.803	24.94	99.93	0.557	8.121
3 U 25°C	372.7	7.99	0.773	20.63	99.96	0.566	7.510
3 U 35°C	376.4	6.12	0.736	17.23	99.99	0.569	6.878

**TABLE 4** Hailwood-Horrobin model. Parameters of the absorption and desorption isotherms as a function of the sample and the temperature of the isotherm: Molecular mass of the monohydrated sample ( $\text{g mol}^{-1}$ )  $M$ , 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  $X_{(p=s)}$  levels where both the primary and the secondary absorption are equal

Reference	$X_m/\%$	$b_0$	$b$	$X_1/\%$	$R^2_{adj}/\%$	$a_{w(p=s)}$	$X_{(p=s)}/\%$
<i>Absorption isotherm :</i>							
OR 15°C	5.09	7.23	0.840	31.21	99.77	0.595	9.129
OR 25°C	4.81	6.70	0.818	25.67	99.86	0.612	8.578
OR 35°C	4.81	5.72	0.794	22.50	99.91	0.630	8.446
3 U 15°C	3.65	8.60	0.856	24.94	99.77	0.584	6.632
3 U 25°C	3.49	7.68	0.834	20.63	99.87	0.599	6.295
3 U 35°C	3.57	6.07	0.800	17.23	99.93	0.625	6.303
<i>Desorption isotherm :</i>							
OR 15°C	6.29	12.96	0.801	31.21	99.89	0.624	11.845
OR 25°C	5.93	10.36	0.777	25.67	99.87	0.643	11.034
OR 35°C	5.68	7.81	0.754	22.50	99.91	0.663	10.354
3 U 15°C	5.03	8.34	0.803	24.94	99.93	0.623	9.174
3 U 25°C	4.83	6.95	0.773	20.63	99.96	0.647	8.692
3 U 35°C	4.78	5.24	0.736	17.23	99.99	0.680	8.386

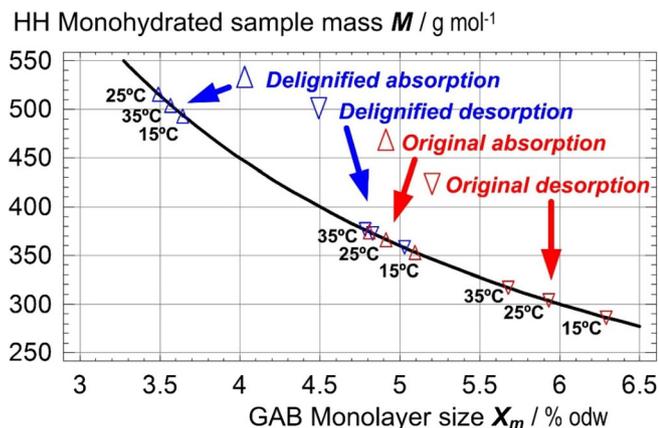
**TABLE 5** Dent model. Parameters of the absorption and desorption isotherms as a function of the sample and the temperature of the isotherm: Monolayer size  $X_m$ , energy constants of the monolayer  $b_0$  and the multilayer  $b$ , regain at saturation  $X_1$  (% odw), determination coefficient of 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

the increase in the size of the monolayer. The greater the temperature was, the smaller the size of the monolayer, although the delignified sample exhibited the smallest monolayer size during absorption, the smallest size was that given by the sample measured at 25°C. The lowest values were those measured on delignified samples during absorption, and the greatest values were measured on the untreated samples during desorption. Intermediate results were given by both the delignified samples during desorption and the untreated samples during absorption, showing that the lower the temperature was, the greater the monolayer size.

#### 4.6.2 | Energy constants of the monolayer

The energy constants of the monolayer for the three models were highly related. The relationship between them, shown in Figure 5 are the following:

1. GAB  $C$  and Hailwood-Horrobin  $K_1:K_1 = C - 1 (r = 1.00)$
2. GAB  $C$  and Dent  $b_0:b_0 = 0.04 + 0.8 C (r = 0.99)$
3. Hailwood-Horrobin  $K_1$  and Dent  $b_0:b_0 = 0.83 + 0.8 K_1 (r = 0.99)$



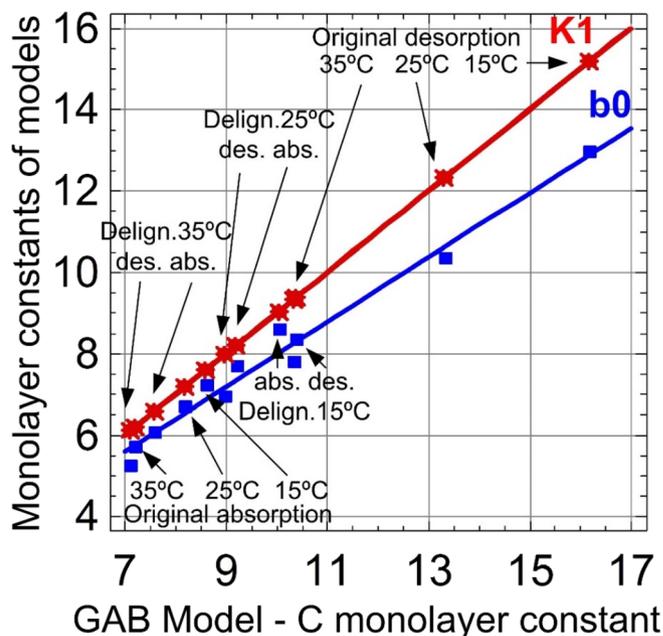
**FIGURE 4** Relationship between two methods estimating the size of the monolayer: That of GAB or Dent models measured as g of water linked to 100 g of dry sample and that of the Hailwood-Horrobin model as the molecular mass of the monohydrated sample in  $\text{g mol}^{-1}$  according to the sample, measuring process and temperature [Color figure can be viewed at wileyonlinelibrary.com]

Lignin causes great differences between absorption and desorption when the energy constant of the monolayer was measured, while temperature made these constants decrease. The delignification greatly reduced differences between absorption and desorption, with the effect of temperature being stronger than that of the measuring process on lowering the energy constant of the monolayer. The range of variation in the monolayer constants was greatly reduced by delignification. The energy constants in the absorption of the delignified fiber were higher than those of the original fibers, while the opposite occurs in desorption.

#### 4.6.3 | 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 untreated samples. The absorption results were higher than those during desorption and decreased with increasing temperature, being the highest and the lowest in delignified samples measured during absorption at 15°C (0.856) and desorption at 35°C (0.736), respectively.

Delignification caused a decrease in regain at saturation of approximately 5.7%, which was also affected by temperature. The highest regain at saturation was observed for the original sample at 15°C (31.21%), while the lowest regain value was observed in the delignified sample measured at 35°C (17.23%).



**FIGURE 5** Relationship between the GAB monolayer constant  $C$  and those of the Hailwood-Horrobin ( $K_1$ ) and Dent ( $b_0$ ) models [Color figure can be viewed at wileyonlinelibrary.com]

#### 4.6.4 | Water activities at which primary and secondary moisture uptake values are equal

Water activity at which primary and secondary moisture uptake values are equal 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. Greater results were given by the Hailwood-Horrobin model, and the highest results were those of the Dent model. The estimations of these two last models depend on the way they separate primary and secondary moisture uptakes, resulting in different levels of water activity at which both primary and secondary moisture uptake 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 with the secondary uptake. The greater the multilayer energy constant  $K$  was, the lower the level at which primary sorption was equal to secondary sorption.

Figure S3 shows these results according to the different models as a function of the energy constant of the multilayer. The supporting information also includes the equations relating the energy constant of the multilayer and the water activity at which primary and secondary sorption are equal according to the models.

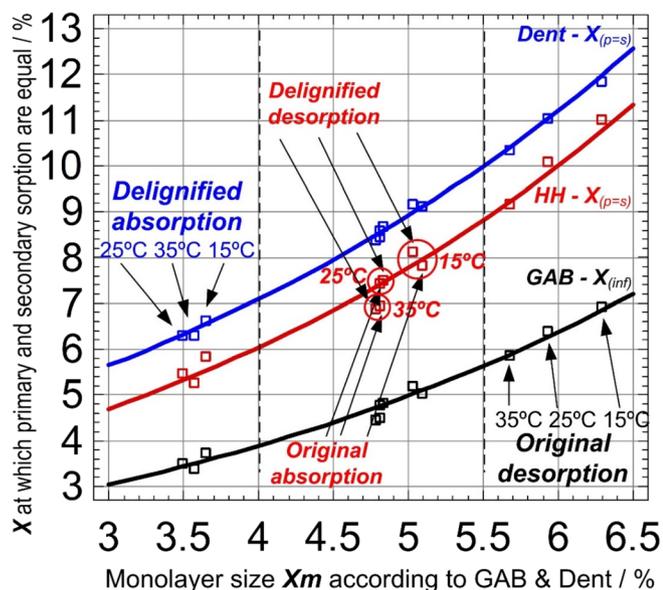
#### 4.6.5 | Regain values at which primary moisture uptake is equal to secondary moisture uptake

Estimations of regain using the three models led to different results: The highest values were those given by the Dent model, closely followed by those of the Hailwood-Horrobin model and the lowest being those given by the GAB model, which were above 50% of the results given by the first two above-mentioned models.

A very strong relationship was observed between these values and the size of the monolayer  $Xm$  estimated by both the GAB and Dent models. Figure 6 shows the relationship between the size of the monolayer  $Xm$  and the values at which primary regain values were equal to those of secondary values according to the three different models.

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

1. Dent model:  $X_{(p=s)} = \text{EXP} (1.0456 + 0.2284 Xm)$  ( $r = 0.998$ )
2. HH model:  $X_{(p=s)} = \text{EXP} (0.7896 + 0.2521 Xm)$  ( $r = 0.986$ )



**FIGURE 6** Relationship between the size of the monolayer  $Xm$  and the estimated regain values where primary and secondary sorption values were equal according to the GAB, H-H, and Dent models [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

3. GAB model:  $X_{(inf)} = \text{EXP} (0.3447 + 0.2461 Xm)$  ( $r = 0.989$ )

The greater the size of the monolayer  $Xm$  was, the higher the regain at which primary and secondary sorption were equal. The highest values of both  $Xm$  and  $X_{(p=s)}/X_{(inf)}$  were those of the untreated samples measured in desorption, showing a significant effect of the temperature on the decrease in these values. In contrast, with the lowest values of  $Xm$  and  $X_{(p=s)}/X_{(inf)}$ , the delignified samples measured during absorption exhibited a very small influence of temperature on the results. Between the two extremes, samples of delignified samples measured during desorption and untreated samples measured during absorption were observed. The results between both types of samples were very similar according to the temperature, with the lowest values measured at 35°C and the highest values measured at 15°C.

#### 4.7 | Enthalpies of primary and secondary bonding

Using the results of the primary and secondary energy constants given by the three fitted models to the absorption/desorption isotherms at three different temperatures, the application of the Kapsalis<sup>25</sup> equation enabled estimation of variation in the enthalpy of water molecules in primary and secondary bonding. The goodness of fit was evaluated by the correlation coefficient between the energy constants and the inverse of the absolute temperature  $1/T$ . The results are shown in Table 6.

The values of the primary constants of the GAB, H-H, and Dent models were similar, although the greatest were those of the GAB model and the lowest those of the Dent model. The secondary constants were the same for the three models. The enthalpies of primary bonding were determined using the isotherm of absorption and that of desorption, giving the results of  $\Delta H_{pa}$  and  $\Delta H_{pd}$  that evaluate the variation in enthalpy caused by the migration of water molecules between the multilayer and monolayer and the effect of hygroexpansion in absorption that modifies the morphology of the fiber. The same occurs with the secondary bonding measured on the absorption or the desorption isotherms, resulting in two estimations of the variation in enthalpy  $\Delta H_{sa}$  and  $\Delta H_{sd}$  caused by the change in water molecules between the multilayer and the environment of free molecules.

Figure 7 shows the results of the enthalpies determined by the energy constants of the models. The enthalpies of primary bonding depended on the model fitted to the absorption/desorption isotherm, although for

secondary bonding, the three models yielded the same constants, resulting in identical enthalpy values. As a matter of comparison, the enthalpy of a hydrogen bond per gram of water<sup>33</sup> ranges from approximately 700 to 1630 J g<sup>-1</sup>, which means that for values of enthalpy reaching these levels, it can be considered that moisture was attached to the sample by hydrogen bonding, and values below the enthalpy of a hydrogen bonding should be attributed to van der Waals forces that normally occur between adjacent molecules.

Moisture absorption and desorption is a dynamic process during which water molecules move the inner sorption sites, completing the monolayer where water was directly linked to the fiber by hydrogen bonds and enabling the growth of the secondary multilayers. Lignin is an easily accessible moisture-absorbing material, although it is not very hydrophilic. In desorption, which occurred after complete absorption, the secondary sorbed molecules near the external surface weakly linked to lignin were the first to migrate to the environment, being progressively followed by the internal secondary sorbed molecules until reaching the primary sorbed

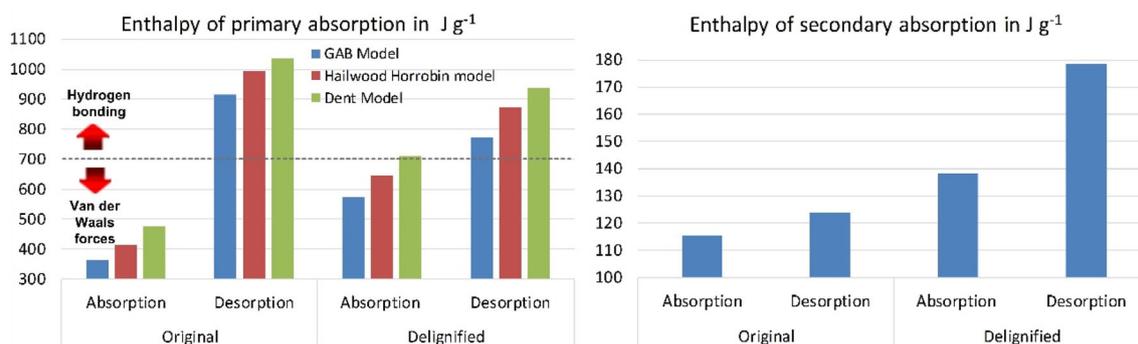
molecules in the monolayer that were the last to be desorbed.

The presence of the higher amount of lignin in the untreated hemp than in the treated hemp can explain the lowest values of absorption enthalpy. In absorption, primary and secondary bonding occur at the same time because the primary sorbed molecules hinders the completion of the most inner reactive sites of the fiber. At the beginning of absorption, a great amount of water links the low-hydrophilicity lignin and the most external cellulose sites, favoring a growth of secondary absorption to these sites, which explains the low measured enthalpies. In desorption, the opposite occurs: water linked to lignin and all secondary sorbed water are easily removed, which explains the highest enthalpies measured for primary bonding between water and cellulose, reaching the enthalpy values attributed to hydrogen bonding.

The lower lignin content of the delignified fiber than of the untreated fiber explains the greater enthalpies of the primary sorbed water that is bonded to more cellulose than lignin, and the lower differences between enthalpies measured during absorption and desorption compared

**TABLE 6** Correlation coefficients  $r$  and variation in enthalpies caused by primary bonding  $\Delta H_p$  and secondary bonding  $\Delta H_s$  of water molecules on original and delignified hemp, estimated from the slope of the straight line fitted between the logarithm of the energy constants and the inverse of the absolute temperature ( $1/T$ ) on the absorption and desorption isotherms

Energy constants of models	$r$ between constants and $1/T$				Variation in bonding enthalpy			
	Absorption		Desorption		Absorption		Desorption	
	OR	3 U	OR	3 U	OR	3 U	OR	3 U
<u>Primary bonding (monolayer):</u>					$\Delta H_{pa}/\text{J g}^{-1}$		$\Delta H_{pd}/\text{J g}^{-1}$	
GAB: $C$	0.963	0.973	0.995	0.988	361.99	573.15	915.96	772.84
HH: $K1$	0.962	0.972	0.995	0.987	414.69	647.55	993.39	873.42
Dent: $b0$	0.976	0.976	0.996	0.991	478.43	711.51	1037.0	938.97
<u>Secondary bonding (multilayer):</u>					$\Delta H_{sa}/\text{J g}^{-1}$		$\Delta H_{sd}/\text{J g}^{-1}$	
$K, b$	0.999	0.989	1.000	0.996	115.39	138.36	123.99	178.38



**FIGURE 7** Enthalpies of primary and secondary bonding given by to the different models used to fit the absorption/desorption isotherms of untreated and delignified hemp in J g<sup>-1</sup> [Color figure can be viewed at wileyonlinelibrary.com]

with those measured in the untreated samples can be easily explained by the dynamics of the process, which requires time for completion.

The enthalpies of secondary absorption were much lower than those of primary absorption. The untreated samples with a greater amount of lignin showed the lowest enthalpies, and differences between absorption and desorption can be explained by the effect of swelling and time needed to complete multilayer formation.

Considering primary and secondary bonding, estimations in desorption showed higher correlation coefficients with energy constants than those in absorption and seemed to be more easily explained in desorption considering the relative amount of lignin and cellulose in the samples.

## 5 | CONCLUSIONS

Processing the results given by the absorption/desorption isotherms made at 15, 25, and 35°C of alkaline delignified and untreated hemp fibers led to the following conclusions:

1. Delignification reduced the sorption ratio of hemp, although lignin plays a determinant role at low water activities, cellulose determined sorption behavior at high water activities.
2. A model was developed that enables the estimation of both the absorption/desorption isotherms at 0°C and the loss of regain caused by temperature. Delignification lowered the effect of temperature on moisture uptake.
3. Hysteresis decreased with increasing water activity. At low water activities, related to molecules of water directly linked to the polymer, the hysteresis of delignified hemp was lower than that of the untreated hemp, while at higher values, the opposite occurred. The greater the temperature was, the lower the hysteresis.
4. Regarding the parameters given by the models fitted to the absorption/desorption isotherms,
  - a. The size of the monolayer measured during desorption was always higher than that measured during absorption. Lignin greatly contributed to the growth of the size of the monolayer, while temperature negatively affects the size.
  - b. The energy constants of the monolayer differed according to the model used. The energy constant values of delignified fiber measured during absorption were higher than those of the untreated fiber, while the opposite occurred during desorption. Lignin caused great differences between absorption and desorption, while the greater the temperature was, the lower the monolayer energy constant.
  - c. The energy constants of the multilayer were identical for the three models, showing a greater range of variation in delignified samples than in the untreated samples. The absorption results were higher than those of desorption and decreased with increasing temperature.
  - d. The water activity at which primary moisture uptake was equal with secondary moisture uptake decreased with the increase in energy constant of the multilayer; thus, the greater the constant was, the lower the water activity at which primary moisture uptake was equal to secondary one.
  - e. The level of regain at which primary moisture uptake was equal to secondary moisture uptake, was strongly related to the size of the monolayer.
5. The higher amount of lignin in the untreated hemp than in the delignified hemp explains the lowest values of sorption enthalpy. Differences in the estimation of sorption enthalpy between absorption and desorption were explained by the role of low-hydrophilicity lignin and the most external cellulose sites during absorption, which made primary absorption difficult while facilitating the removal of secondary water in desorption, resulting in higher values of enthalpy of bonding between water and cellulose, reaching enthalpies attributed to hydrogen bonding.
6. The enthalpies of secondary absorption were much lower than those of primary absorption. The untreated sample with a greater amount of lignin showed the lowest enthalpies, and differences between absorption and desorption could be explained by the effect of swelling and the time needed to complete multilayer formation.
7. Considering primary and secondary bonding, estimations during desorption showed higher correlation coefficients with the energy constants and seemed to be more easily explained considering the relative amount of lignin and cellulose in the samples.

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