

Application of the Guggenheim, Anderson, de Boer equation to study the impact of sealing treatments on pine wood sorption characteristics

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Abstract

Surface treatments can modify the materials behavior toward water sorption phenomena. The Guggenheim–Andersen–de Boer sorption equation, already used in the past to study various wood species, is here proposed to investigate the sorption behavior of pine wood samples treated with different sealing material. Particularly, the paper aims to explore the modification of the k parameter with the applied coating. Measurements of sorption–desorption branches permitted to clearly distinguish the behavior of treated samples, the relative humidity (RH) conditions over which they are more dimensionally stable, as well as their tendency to swell and shrink. The proposed study permitted to evaluate the usefulness of the k parameter as an indicator of the presence of chemical treatments on wood at high RH values. Particularly, the k value has been found to change as a function of chemicals surface treatments limiting in different ways the access and expulsion of water moisture.

Highlights

- Surface sealed pine wood samples were analyzed by vacuum microbalance.
- The Guggenheim–Andersen–de Boer equation has been applied to water sorption–desorption data.
- The equilibrium moisture content and its first derivative explained samples swelling/shrinking tendency.
- Assessment of the usefulness of k as indicator of the wood treatment at high relative humidity values.
- Assessment of k modifications in relation to the type of sealing treatment.

KEYWORDS

GAB equation, pine wood, sealing treatments, microbalance, water sorption, high RH

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1 | INTRODUCTION

Modification in ambient temperature and relative humidity (RH) affects the equilibrium moisture content (EMC) of hygroscopic materials as wood. The EMC can be considered as material parameter describing the binding potential of water to this adsorbent material. An excess or a pauperization of water vapor adsorbed or desorbed by the material modifies its EMC as well as its swelling or shrinking rate and consequently its dimensions. On the long-term wood kept at high, low conditions of RH or exposed to RH fluctuations will be subjected to a high level of risk of decay. Therefore, an accurate estimation of wood response to moisture variation can permit to determine RH conditions with lower risk of environmentally induced damage. Similarly, a deep understanding of the wood–water relationship after surface treatments can further help in assessing the service life of conservation treatments or to plan additional maintenance for materials treated with short-lasting treatments under the same or similar environmental RH conditions.

Many different chemicals are currently used to preserve wood surfaces as well as to modify its properties, generally depending on the final application foreseen for the material. In particular, the chemical modification of wood has been mainly attempted in order to improve its dimensional stability resulting from changes in moisture content. Among many treatment methods, the most popular are heating,^{1,2} impregnation with monomers polymerizing inside the material, or functionalization.³ It is generally possible to distinguish improved wood or densified wood, modified by densification/resin impregnation, from materials submitted to cell-modification processes, occurring by reactive chemicals.³ Only in this case it is possible to define the process as a chemical modification because chemical reactions occur between reactive parts in the wood and a reagent.

Different approaches have been proposed depending on the property to be modified: for water repellency, a reduction of the hydrophilic nature of wood is usually carried out by bonding on hydrophobic groups. The improvement of dimensional stability can be achieved by bulking cell walls with bonded chemicals, or using cross-linking polymers limiting cell wall expansion, or bounding functional group that can increase hydrophobicity. Another often desirable effect is flame retardance achievable by bonding retardants or flame suppressants functional groups to the cell walls. Similarly, ultraviolet (UV) resistance can be obtained by bonding UV blockers or absorbers to lignin.⁴

As stated above, most of the applied treatments are commonly aimed to limit variations in the material moisture content, and this can be done acting on the mechanism of water absorption. Moisture sorption process in wood has been described by the Hailwood and Horrobin equation that in turn has been demonstrated to be equivalent to the Guggenheim–Andersen–de Boer (GAB) sorption equation.^{5,6}

The latter equation can describe the full shape of type II isotherm^{5,7} covering an activity range (a_0) much wider than that of models such as the Brunauer–Emmett–Teller (BET) equation.⁷ This is due to the fact that the theoretical basis for the GAB sorption isotherm fits with the vapor adsorption in porous bodies as wood because of the bonds forming between water molecules and wood hydroxyl groups.⁸ When additional water layer is deposited, the interactions with the sorbent surface are assumed to be weaker until reaching the energy level of liquid water.^{9–12} In addition to the BET equation, the GAB one introduces a further parameter indicated as k , related to the difference of the standard chemical potential between molecules creating the additional adsorbed layers and those in the liquid state.⁷

This work focuses on the application of GAB equation as an alternative to other water sorption-based models available in literature¹³ (e.g., the Langmuir, the BET, the Oswin, and the Halsey models). In particular, the model has been applied to interpret the sorption data obtained from pine wood samples, which tangential–radial (TR) surfaces were coated with different sealing materials. The RH-dependence differences in the moisture content of the tested samples (one standard—without any treatment—and five treated) has been explained, and the GAB water sorption isotherms have been used to

- 1 investigate how the GAB parameters can change when fitting water vapor sorption data for the six tested pine samples,
- 2 understand the moisture-induced response of coated wood in general (Sections 3.1 and 3.2),
- 3 study the behavior of the GAB k constant obtained for all tested pine samples as it has never been studied in detail in literature.

2 | MATERIALS AND METHODS

During this study, the adsorption branches of the water vapor isotherms were measured for six small samples cut from pine wood slices. The original pine log—constituting the material for the experiments—was grown, cut, and naturally air

dried in the Trøndelag area over a 3-year period. Then from the log, radially cut pine slices (dimensions of $20 \times 10 \times 2$ cm) were prepared, and five of them were treated on the TR surfaces with the following chemicals:

- Paraloid B72 40% (w/v) (P40) deposited using a brush,
- Cellulose sand seal (CS) spray (Chestnut),
- Paraloid B72 40% (w/v) deposited over a dried cellulose sand seal layer (CS + P40),
- Renaissance microcrystalline wax (R) deposited with a spatula,
- Epoxy resin (E), containing bisphenol A diglycidyl ether as epoxy component (the hardener is not specified) deposited with a spatula.

As reported in other works¹⁴ currently *in press*, chemicals were tested in order to select the most suitable treatment for further experiments involving the stress development induced by moisture gradients appearing in coated wood under high RH changes (50%) and further investigations of its damage induced by such stress dynamics.

The last pine sample was instead kept clean, that is, not treated with chemicals on the surface to maintain a standard reference during the tests. Measurements of the water vapor sorption on the six samples were carried out following the dynamic gravimetric method at room conditions (i.e., 24°C) with the aid of a vacuum microbalance (CI Electronics Ltd.) through a continuous measuring procedure. During the process, water vapor was introduced (or removed) at a slow constant rate of 0.01 Torr/min to keep quasi-equilibrium conditions while the changes in weight were detected within the full range of water vapor relative pressures. Samples were considered to have reached “equilibrium” only when the weight changes were less than 0.05% over 40 min. In the application of the gravimetric technique, special attention has been devoted to reduce at minimum the sources of potential errors, mainly caused by unprecise measurements of pressure (i.e., higher than ± 10 Pa), lack of determination of outgassed weight of the adsorbent either before or after the adsorption measurements, or low attention in controlling measurement of the adsorbent temperature. For details on the experimental procedure and time using the microbalance with wooden samples, see Bertolin et al.¹⁵ From the experiments, the M_{ads} (i.e., adsorption mass) values were calculated based on the initial weight of the outgassed samples. Then these outcomes were further elaborated to calculate the volume of adsorbed water (i.e., V_{ads} [cm^3/g of wood_{dry}]) in relation to the water activity or RH (%) using the GAB equation (Equations 1 and 2).

$$V_{\text{ads}} = \frac{V_m C k \frac{RH}{100}}{\left(1 - \frac{kRH}{100}\right) \left[1 + (C-1) \frac{kRH}{100}\right]}, \quad (1)$$

$$\frac{p}{p_0} = \frac{RH}{100}, \quad (2)$$

where V_m is the monolayer capacity, C and k are the adsorption GAB constants, and p and p_0 (Equation 2) are respectively the partial water vapor experimental pressure and its value at saturation. The GAB constants C and k help in identifying the sigmoidal shape of the isotherm functions as reported in Section 3. The mathematical model behind this type of isotherm, besides describing in detail the sorption behavior at $RH < 93\%$, has a strong theoretical background with parameters that may explain the sorption processes (further refinement of the Langmuir and BET models of physical adsorption). The GAB mathematical model is representative of microporous materials where unrestricted monolayer–multilayer adsorption at the internal surface of a material exists. The state of the sorbate molecules in the second layer is identical to that one in superior multilayers but different from that of the monolayer below (directly bound to the wood hydroxyls) or of the liquid state molecules on the top of the multilayers. Therefore, as stated in Andrade et al.,¹³ C_{GAB} coefficient represents the water primary layer binding strength (with respect to the multilayers^{15,16}) at the sorption sites at a certain T value (24°C = 297.15 K). The correcting factor k_{GAB} , with p_n being the partial water vapor pressure of multilayers, describes a less structured state of the sorbate in multilayers (on the top of the monolayer) than in the sorbate's pure bulk liquid state^{7,15,17}:

$$k_{\text{GAB}} = \frac{p_0}{p_n} < 1. \quad (3)$$

Details concerning the physical meaning of the C and k parameters are reported in Data S1.

3 | RESULTS AND DISCUSSION

A preliminary characterization of the coated surfaces has been described in previous works¹⁴ currently *in press* and involved the evaluation of (a) surface homogeneity, penetration of chemicals, and treatment thickness using both optical and electron microscopy; (b) color variation of the samples' surfaces caused by the coating with a spectrophotometer and a spectrophotometric scanner; (c) surface wettability by means of static contact angle measurements.

This work, instead, analyzes and discusses in details the obtained sorption–desorption data, evaluating the type of adsorption isotherms and hysteresis measured for the six tested samples, the way water molecules are bound in the wood structure at different RH conditions, and finally discussing the possible reasons, which explain the observed effects, comparing our findings with those currently *in press* and available in literature.^{5,18–20}

3.1 | Adsorption isotherms types and GAB constants of the analyzed samples

In 1940, Brunauer et al.²¹ was the first who classified sorption isotherms in five types based both on their shape and on their physico-chemical processes influencing these shapes. In this study, the analysis of experimental data (reported in Table 1) compared with literature results^{22–24} reports that all the samples show isotherms of type II²¹ with GAB-like sigmoidal shape with overall determination coefficient $R^2 > 0.999$ because $C_{GAB} > 5.76^{23}$ (except epoxy resin) and $0.24 < k_{GAB} < 1$.

Table 1 reports the V_m coefficients calculated from the GAB fit per each tested sample. It is representative of the minimum water monolayer (or minimum moisture content) covering the active hydrophilic binding sites on the sample under examination. It provides information on possible risk of decay caused by variation (increase) of moisture content in the material or, in our case study, on the material service life after the treatments. This is mainly linked to the possibility of having available reactive sites on the sample surface, a characteristic that can be modified by the presence of surface treatments. Generally, V_m values decrease with higher temperature or due to a change on physico-chemical characteristics as in this study. Treated pine samples show, in fact, a V_m decrease of up to approximately 22% with respect to the reference clean sample. These findings indicate a lower availability of active hydrophilic bonding site on treated samples, except in the case of epoxy resin (E) with instead shows a V_m value comparable with the untreated pine sample. In particular: P40 and P40 + CS show similar decreasing effects highlighting the same service life horizon, basically because the final surface to be considered is P40 based for both samples; the wood surface treated with the sprayed cellulose sand spray (CS) displays the maximum decrease in water accessing to primary sorption sites; an intermediate decrease is observed for the sample treated with the Renaissance microcrystalline wax (R).

In Figure 1 the treatments effects on C_{GAB} and k_{GAB} for adsorption branch of isotherms are reported. The effect of the treatment on C_{GAB} can be expressed by Equations 4 and 5

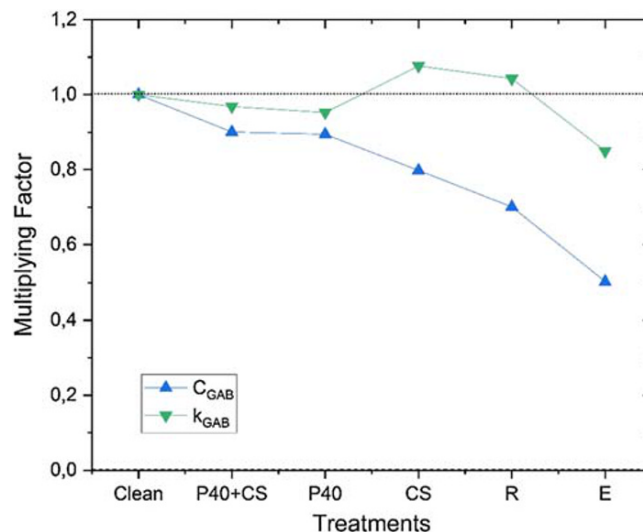
$$C_{GAB,treated} = C_{GAB,untreated} \cdot C_{GAB,chemical} \quad (4)$$

$$\frac{C_{GAB,treated}}{C_{GAB,untreated}} = C_{GAB,chemical} = C_{0,chemical} \exp\left(\frac{H_0^I - H_n^I}{RT}\right) \quad (5)$$

TABLE 1 Guggenheim–Andersen–de Boer (GAB) parameters (V_m , A_{ds} , C_{GAB} and k_{GAB}) and their determination coefficient (R^2) as obtained by experiments with the microbalance on the five treated samples (i.e., P40, CS, R, E, and P40 + CS) and the untreated reference standard (clean)

Treatment	V_m (cm ³ /g)	C_{GAB}	k_{GAB}	R^2
Clean	0.061 ± 0.001	8.530 ± 0.530	0.758 ± 0.005	0.999
P40 + CS	0.057 ± 0.001	7.680 ± 0.330	0.734 ± 0.004	0.999
P40	0.056 ± 0.001	7.630 ± 0.170	0.722 ± 0.002	0.999
CS	0.048 ± 0.001	6.810 ± 0.510	0.816 ± 0.004	0.999
R	0.052 ± 0.002	5.980 ± 0.640	0.791 ± 0.008	0.999
E	0.062 ± 0.003	4.280 ± 0.340	0.644 ± 0.014	0.999

FIGURE 1 The Guggenheim–Andersen–de Boer (GAB) constants C and k_{GAB} of the five treated (i.e., P40, CS, R, E, and P40 + CS) samples and of the untreated (clean) sample



Therefore, from Table 1 and Figure 1 (blue dataset), comparing C_{GAB} of the treated samples with the untreated one, a damping factor can be clearly visible. Except for the correction provided by the entropic accommodation factor (i.e., $C_{0,chemical}$), the overall observed effect on the measurements represents the modification of the molar sorption enthalpies of multilayers (on top of the monolayer) with respect to that of the monolayer of water, in this specific case caused by the application of chemicals. This is due to a change, generally a weakening, of the bonds formed between water and the primary sorption sites on treated surfaces with respect to what happens on clean wood. Consequently, a decrease in the C_{GAB} can be interpreted that treated surfaces are adsorbing water molecules less strongly than untreated wood. In other words, it can give indication on how and how strongly molecules creating the very first water layer bound to the sample surface are in turn bound to molecules creating the successive water layers. Modifications of values reported in Table 1 can be interpreted considering the strength of chemical bonds forming between the samples surfaces and the first water monolayer.

In untreated wood, hydrogen bond forms between the material hydroxyl groups and water molecules. In this case, dipoles form because the electronegative oxygen atoms attract hydrogen valence electrons acquiring a partial negative charge ($O^{\delta-}$) and leaving partial positive charges on such atoms ($H^{\delta+}$). At the same time, these $H^{\delta+}$ are attracted by $O^{\delta-}$ of other water molecules creating the H bonds whose strength is comparable with that of bonds formed with the primary sites on wood. In case of treatments, when water molecules interact with materials having CH_2/CH_3 terminal groups, that is, when a polar liquid is deposited on a nonpolar surface, only weak interactions are possible due to the extremely weak dipole-induced dipole attractions. A slight shift in the center of gravity of the negative partial charge on the water molecules creating the first water layer occurs; thus, consequently, bond formed with water molecules in the following layers become weaker than normally expected. In other words, after treatments, the monolayer of water binds more weakly to primary sorption sites^{20,25} and consequently less energy (heat) is necessary to break such weak bonds and remove water molecules.

More specifically, the values found for P40 and P40 + CS show a variation of approximately -10% with respect to untreated wood, while the strength of bonds formed on the surfaces of samples treated with cellulose sand spray (CS), Renaissance microcrystalline wax (R), and epoxy resin seem to gradually decrease.

Similarly, the effect of the treatment on k_{GAB} can be expressed by Equations 6 and 7.

$$k_{GAB, treated} = k_{GAB, untreated} \cdot k_{GAB, chemical}, \quad (6)$$

$$\frac{k_{GAB, treated}}{k_{GAB, untreated}} = k_{GAB, chemical} = k_{0, chemical} \exp\left(\frac{H_0^I - H_n^I}{RT}\right), \quad (7)$$

and it is associated to the relation existing between the already formed multilayer and water deposited entirely in its liquid phase. C_{GAB} is found to be an order of magnitude higher than k_{GAB} describing a higher sorption heat of the

monolayer compared with the multilayer.²⁶ The change in k_{GAB} coefficient on treated samples (green dataset in Figure 1) shows two different tendencies depending on the type of applied chemicals:

- 1 A decrease, indicating a less favorable situation to surface saturation, means the amount of sorbed water vapor is lower than the “idealized” case at RH = 100%. This is the case observed with Paraloid-coated surfaces (P40 and P40 + CS) and at the maximum extension with the application of epoxy resin (E) treatment. Such behavior was interpreted by Timmermann in 2003⁷ as a demonstration of less stable and structured state of the multilayers.
- 2 An increase in the dewpoint temperature (T_{DP}), which reduces the dew point spread, that is, the difference between T_{DP} and the T , creating a more favorable situation to saturation. This was observed for samples treated with Renaissance wax (R) or the cellulosed sand layer sprayed alone (CS) that highlights a possibly more structured state of water multilayers.

3.2 | Analysis of EMC variation and hysteresis caused by the treatments

As widely reported (see, e.g., Almeida et al.²⁷) the water sorption in wood, relates to two types of water, that is, the bound and free water. The first is adsorbed on the wood cell walls, while the second mainly fills in the wood lumen.²⁷ The relative proportions between these types of water are in relation with the EMC of wood that is sensitive to changes in p/p_0 (and T). Figure 2 reports the isotherms of six tested samples (i.e., p/p_0 vs. EMC adsorption and desorption branches at $T = 24^\circ\text{C}$). As generally observed (top panel), both adsorption branches and desorption branches of treated samples have lower EMC than the clean sample. A possible reason of that, as reported in Broda et al.,²⁰ could be the different saturation pressures of the used chemicals lowering the EMC values expected for the treated wood samples.

TABLE 2 Parameters ($V_{m, Ads}$) as obtained by experiments with the microbalance on the five treated samples (i.e., P40, CS, R, E, and P40 + CS) and the untreated reference standard (clean) and as calculated from the first derivative of equilibrium moisture content with respect to p/p_0 ($\pm 10\%$) as reported in Figure 2

Treatment	EMC _{ads} at $\frac{\partial EMC}{\partial \left(\frac{p}{p_0}\right)} = 0$	Min p/p_0 (%)	$V_{m,ads} - V_{ads \text{ at min}}$	$\frac{V_{m,ads} - V_{ads \text{ at min}}}{V_{m,ads}}$ (%)	$V_{ads \text{ at } p/p_0 \text{ min}}$
Clean	14.66 ± 1.47	20	0.019 ± 0.01	30.2 ± 0.02	0.043 ± 0.01
R	12.40 ± 1.24	40	0.004 ± 0.01	5.94 ± 0.06	0.049 ± 0.01
P40 + CS	11.53 ± 1.53	50	-0.017 ± 0.01	-30.2 ± 0.02	0.074 ± 0.01
P40	11.48 ± 1.15	40	-0.0040 ± 0.01	-6.59 ± 0.02	0.060 ± 0.01
CS	10.88 ± 1.09	40	-0.007 ± 0.01	-11.26 ± 0.02	0.055 ± 0.01
E	10.43 ± 1.04	30	0.023 ± 0.01	38.14 ± 0.07	0.038 ± 0.02

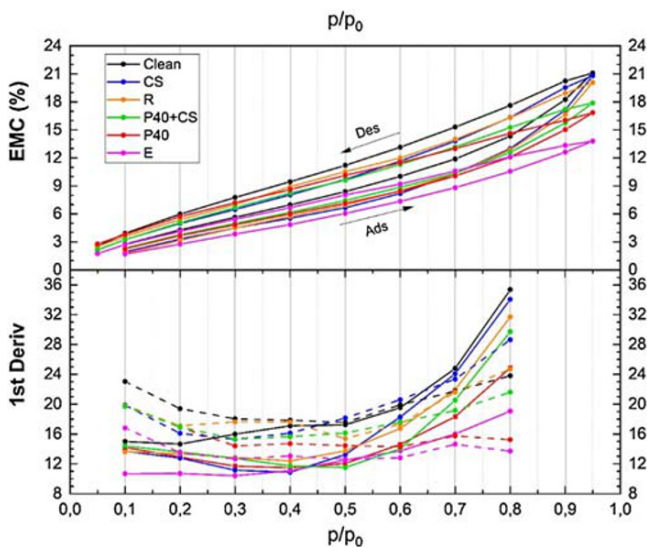


FIGURE 2 Top: equilibrium moisture content (EMC) for the isotherms (adsorption/desorption branches) of 6 tested samples: clean (black), CS (sealed spray—blue), R (Renaissance microcrystalline wax—orange), P40 + CS (Paraloid above the cellulose sand seal spray layer—light green), P40 (Paraloid—Red) and E (epoxy resin—violet). Bottom: First EMC derivative respect to p/p_0 for the same datasets. Solid lines: sorption branches; dashed lines: desorption branches

The results reported in Table 2 helps in the analysis of the wood–water interactions as follows.

In the clean wood, the monolayer saturation moisture content in adsorption ($V_{m,Ads}$) is equal to $0.061 \text{ cm}^3/\text{g}$. This is the maximum amount of water taken by the environment on the sample via monolayer sorption. The point after which multilayer sorption starts to prevail is highlighted in Figure 2 (bottom panel) by the minimum of the derivative of the EMC in relation to p/p_0 and corresponds to the value $V_{Ads} = 0.043 \text{ cm}^3/\text{g}$, occurring at 20% RH (min p/p_0 in Table 2). This indicates that from 20% to 100%, the water adsorbed on the untreated sample via monolayer sorption is approximately 0.01858 (or 30%). The minimum of the derivative falls at 30% RH for E, displaying a water adsorption via monolayer of about 12%, and at 50% for CS + P40, while for the other samples, the minimum of the curve is reached at 40% RH. In the case of the microcrystalline wax treatment (R), a behavior similar to that of clean wood is observed with about 6% of water adsorbed on sample via monolayer.

At the opposite, P40 and CS deposited alone and together, does not show any additional uptake of water via monolayer but rather that already within the inflection point (i.e., 40% and 50% RH) the multilayer sorption is the prevailing phenomenon.

In addition, Figure 2 (bottom panel) reports interesting information on the first derivative that is the rate of EMC change with RH depending on the treatment. The first derivative can be defined as a sort of moisture coefficient, which exemplifies the propension to contraction (negative slope of the first derivative in Figure 2—bottom panel—at low RH levels) or to expansion (positive slope of the first derivative in Figure 2—bottom panel—at higher RH levels) of the tested samples when the RH is changing. When considering the adsorption branch, it highlights that—in expansion—the cellulose sand seal spray layer (CS) has the fastest EMC change rate, that is, 0.58% each 1% in RH while the Renaissance wax 0.48%; the three samples (i.e., clean, CS, and P40-coated samples) have a similar rate, that is, 0.37%, 0.33%, and 0.30%; and finally, the epoxy resin has the slowest rate of EMC change with 0.17% each 1% in RH.

While in contraction, the fastest EMC change rate is -0.12% each 1% in RH for Paraloid coupled with cellulose sand seal layer (P40 + CS), followed by the group of untreated, treated with P40 and CS samples with -0.09% each 1% in RH. The most stable sample in shrinkage is that treated with the epoxy resin. The minimum response of the samples is generally within $30\% < \text{RH} < 40\%$.

Looking at the desorption and adsorption branches of the isotherms, the most remarkable alterations of the hysteresis have been calculated per each tested sample with Equation 8:

$$\Delta \text{EMC}_{\max} = (\text{EMC}_{\text{des}} - \text{EMC}_{\text{ads}})_{\max}, \quad (8)$$

and related to the corresponding p/p_0 (i.e., RH) condition. ΔEMC , over the whole range of partial pressures used in the experiments, is shown in Figure 3A, and Table 3 reports the results as follows:

- The untreated pine, the sample treated with the seal spray (CS) alone and coupled with Paraloid (P40 + CS), and the microcrystalline wax (R) have the largest hysteresis at 70% RH and range from 3.41 to 3.68 g/kg going from the

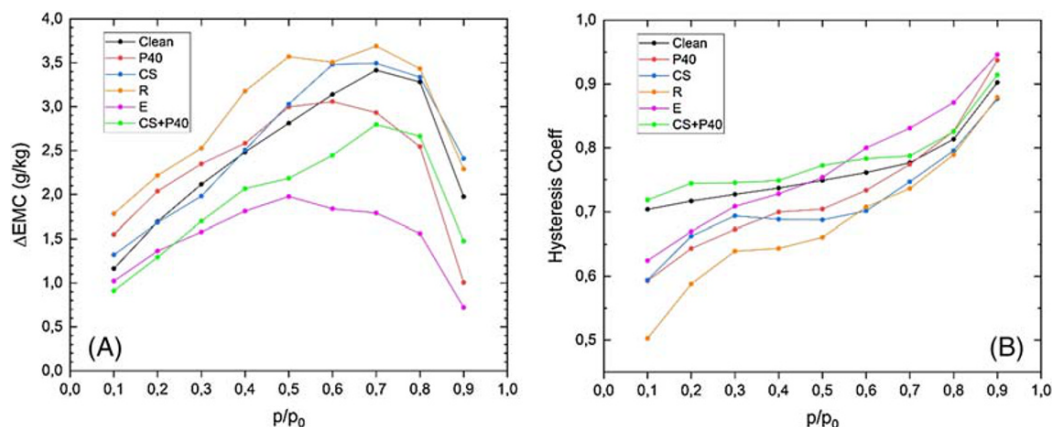


FIGURE 3 (A) The alteration of the hysteresis (ΔEMC) and (B) the hysteresis coefficient for the six tested samples: clean (black), CS (sealed spray—blue), R (Renaissance microwax—orange), P40 + CS (Paraloid above a cellulose layer—light green), P40 (Paraloid—red), and E (epoxy resin—violet)

TABLE 3 Parameters to assess the hysteresis alteration as maximum difference between desorption and adsorption branches and the corresponding p/p_0 ($\pm 10\%$) value.

Treatment	ΔEMC (g/kg)	p/p_0 (%)
Clean	3.42 ± 2.68	70
CS	3.49 ± 2.18	70
P40	3.06 ± 2.30	60
P40 + CS	2.80 ± 2.4	70
R	3.69 ± 2.48	70
E	1.98 ± 2.08	50

untreated to the R sample, while the combination of Paraloid and seal spray shows a difference in the hysteresis of 2.80 g/kg.

- The Paraloid alone (P40) at 60% shows a similar hysteresis of 3.06 g/kg.
- The epoxy resin (E) at 50% the lowest one with 1.98 g/kg.

In Figure 3B, the hysteresis coefficient (Equation 9) is reported:

$$\text{hysteresis coeff} = \frac{EMC_{ads}}{EMC_{des}} \quad (9)$$

Hysteresis are similar for epoxy resin (E) and Paraloid (P40) treated samples, while wood treated with the seal spray (CS) has some similarities with that coupled with Paraloid (CS + P40); a halfway behavior between the two groups is shown by the R sample.

3.3 | Water sorption in pine at low and high value of RH and discrimination of chemical treatments on the surfaces

In literature, the water vapor sorption has been used to estimate specific surface area of materials by adaptation of the approaches exploiting the advantages available in modeling methods.^{28–32} Similarly, in this section, the GAB model has been used to further analyze the water sorption behavior on treated and untreated wood basing on the calculation of the water film thickness t_{GAB} (Equation 10), that is, the thickness of the water layer adsorbed by wood:

$$t_{GAB} = \frac{V_{ads}}{S_{GAB}}, \quad (10)$$

where V_{ads} is obtained using the whole water vapor sorption isotherms fitted to the GAB model and S_{GAB} is the specific surface area calculated per each sample from Equation (11):

$$S_{GAB} = V_m \rho N \frac{\sigma}{M} \quad (11)$$

with N , the Avogadro number, ρ , the water density, σ , the average area occupied by one water molecule in the complete monolayer (0.114 nm^2), and M , the water molar mass of Timmermann and Almeida et al.^{7,27} Similarly, the direct measures obtained with the help of microbalance (i.e., the $V_{ads} - p/p_0$ isotherms) can be expressed in terms of water film thickness with a simple linear plot as it results from Equation 11 and is shown in Figure 4. The variation of S_{GAB} value is linked to the distance between clusters of water molecules on the treated surface: The more the distance increases, the more the S_{GAB} value decreases.

Looking at the set of values of the specific surface area of the tested samples obtained from the GAB model application reported in Table 4, the lowest values were found for CS and R surfaces: observing also the results previously

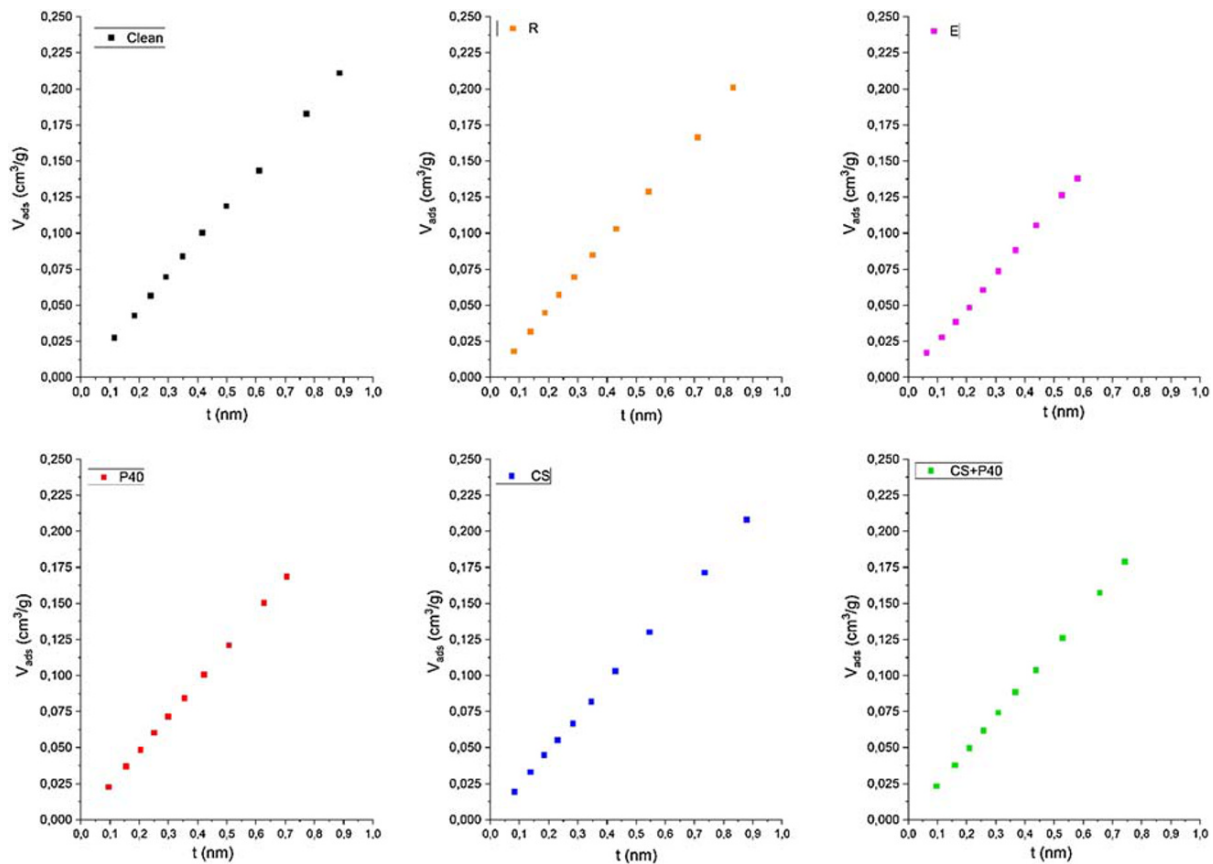


FIGURE 4 $V_{\text{ads}}-t$ relationship for the tested pine samples: clean (black), R (Renaissance microcrystalline wax—orange), E (epoxy resin—violet), P40 (Paraloid—red), CS (sealed spray—blue), and P40 + CS (Paraloid and cellulose sand seal layer—green)

TABLE 4 Specific surface area of untreated and treated wood (i.e., clean, CS, R, P40 + CS, P40, and E) as obtained from the Guggenheim–Andersen–de Boer analysis of sorption data

Treatments	S_{GAB} (m^2/g)
Clean	233.4 ± 0.2
E	234.9 ± 0.7
P40 + CS	216.6 ± 0.2
P40	213.2 ± 0.1
R	198.2 ± 0.3
CS	184.0 ± 0.2

reported in other publications currently *in press*.¹⁴ These treatments displayed the highest static contact angle values, so it seems reliable to hypothesize that the deposited coatings promote the formation of smaller water droplets that tend to remain more distant from each other. At the opposite, as the epoxy resin is a hydrophilic substrate, water molecules tend to form bigger and closer clusters. In the first case, cohesion forces within water molecules will prevail on the adhesion forces between water molecules and the substrate. Such behavior of S_{GAB} is inversely proportional to k_{GAB} : The highest S_{GAB} values correspond to the lowest k_{GAB} ones. Linking k_{GAB} to the strength of bonds existing between the water multilayer and final layer of water in the liquid phase; the connection with the surface wettability properties seems to be supported.

Figure 5 highlights as on the final part of the isotherm (i.e., $p/p_0 > 0.8$ or $\text{RH} > 80\%$) the use of the GAB model better explains as the water vapor accessible on surface layer of treated samples is already grouped together in multilayers as the Pearson's coefficient of the linear fit R_{GAB} is equal to 0.99 at $\text{RH} = 90\%$. (right side). At the opposite, the GAB model underestimates the water thickness of the monolayer at low RH, that is, $<30\%$ especially

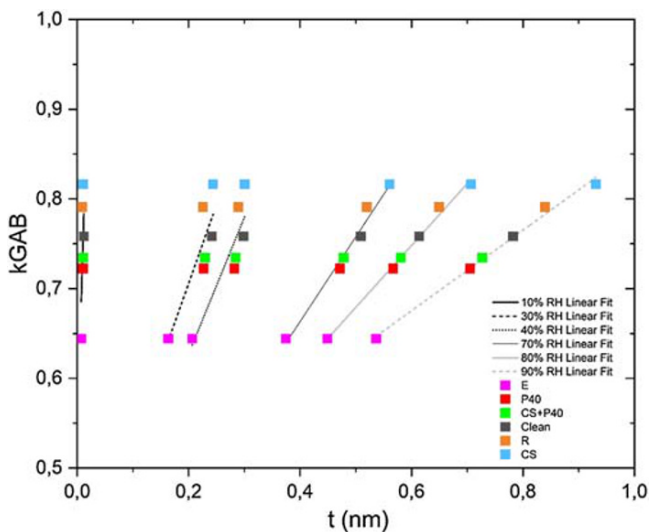


FIGURE 5 k_{GAB} - t relationship for water thickness layer obtained from the Guggenheim–Andersen–de Boer (GAB) model fitted on the sorption data at experimental condition of 10% (black thick line), 30% (black dash thick line), 40% (black short dash thick line), 70% (black thin line), 80% (dark gray thin line), and 90% (dark gray thin dash line) of RH. Samples: clean (black), R (Renaissance microcrystalline wax—orange), E (epoxy resin—violet), P40 (Paraloid—red), CS (sealed spray—blue), and P40 + CS (Paraloid and cellulose sand seal layer—green)

for the samples treated with microcrystalline wax (R) and the cellulose sand seal (CS) on the sample surfaces are chemically less grouped together.³²

4 | CONCLUSIONS

The presented study proposed the application of the GAB equation to investigate the monolayer water content as well as specific surface area of wood from water sorption of untreated pine wood used as standard reference in comparison with samples coated with different materials able to limit the penetration/expulsion of moisture through the radial surface. In particular, a cellulose sand seal spray alone or coupled with Paraloid B72 at 40%(w/v), a microcrystalline wax and an epoxy resin were tested.

Analysis carried out by means of a vacuum microbalance highlighted differences in terms of water content on the samples modified at the surface with chemicals. In particular, the modification of the k_{GAB} parameter as well as of V_{ads} , C_{GAB} , and S_{GAB} were here carefully evaluated. Differences observed in case of coated samples with respect to the untreated one could be explained in terms of lower availability of active hydrophilic bonding sites, strength modifications of the chemical bonds formed between the surface and first water layer, and consequently between it and the following ones up to the last deposited layer entirely considered as water in the liquid phase. At the same way, the chemistry of modified surfaces strongly affected their wettability and the capability of water molecules to aggregate in clusters more or less distant from each other. Then, the analysis carried out on EMC variation and hysteresis of isotherms on samples reported the RH ranges within which treated wood could additionally uptake water via monolayer as well as their different rates in shrinkage and swelling at different RH conditions.

Finally, results clearly highlights as, working at partial pressure condition higher than 0.8 (the last part of the isotherm, that is, $p/p_0 > 0.8$ or RH > 80%), the corrective GAB factor k_{GAB} results particularly useful in discriminating the water vapor uptake on the material surface (expressed as thickness of the water film). This is shown by the k_{GAB} - t relationship that clearly distinguishes the type of chemicals in relation to their rate of moisture uptake, indicative of their propensity for grouping in multilayers and of their binding strengths.

As evident, the reported results clearly showed for the first time how the GAB parameters can be used in the study of wooden materials in order to obtain useful information about their behavior toward water in both its vapor state and its liquid state. Additionally, it has been demonstrated how modification in these values can help discriminating if wooden materials have been chemically treated or not and what class of chemical was used.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

C. Bertolin is responsible for data elaboration—interpretation, writing, and acquisition of financing. L. de Ferri is responsible for sample preparation, data interpretation, and writing. M. Strojceki is responsible for data acquisition—elaboration and review of the content.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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