### **ORIGINAL**



# **Water vapor sorption characteristics and hysteresis of earlywood and latewood within the same growth ring of** *Catalpa bungei*

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# **Abstract**

*Catalpa bungei* is an economically important native hardwood in China whose hygroscopic behavior is vital for industrial applications as it infuences the fnal product's dimensional stability and mechanical properties. In this study, the adsorption and desorption behavior of earlywood and latewood in the same growth ring of *C*. *bungei* wood samples was documented using a dynamic vapor sorption resolution and analyzed using the Guggenheim–Andersen–de Boer (GAB) model. The earlywood and latewood exhibited varying sorption isotherms and hysteresis degrees, and the reasons were analyzed in terms of structure and chemical composition (mainly hemicellulose and lignin). The infuence of benzene–alcohol extracts and vessels on sorption characteristics was also examined. The GAB model perfectly fts the experimental data ( $R^2 \geq 99.7\%$ ) over the full relative humidity range. Specifically, parameters such as the internal specifc surface area of wood can be obtained from the GAB model to help explain the diferences in sorption properties between earlywood and latewood. The maximum water content bound to the primary sites for earlywood and latewood is 6.87% and 7.47%, respectively. Correspondingly, two internal specifc surface areas are 261 m<sup>2</sup>/g and 284 m<sup>2</sup>/g, respectively. The adsorption isotherms of earlywood and latewood in *C*. *bungei* cannot be fully classifed as type II.

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### **Introduction**

Moisture content is an important factor afecting wood's performance and utility. The wood–water relation, including the adsorption/desorption behavior, is still the focus of research both from theoretical and practical points of view (Hill and Xie [2011](#page-13-0); Hill et al. [2015;](#page-13-1) Salmén and Larsson [2018](#page-14-0); Chen et al. [2020](#page-12-0); Hou et al. [2022\)](#page-13-2). Meanwhile, the wood structure is highly heterogeneous and hierarchically organized; therefore, the moisture sorption behavior of wood in response to relative humidity (RH) variations is complex (Bonnet et al. [2017](#page-12-1)). Several studies have shown that the sorption isotherm difers between wood species (Popper and Niemz [2009;](#page-14-1) Albrektas and Ukvalbergienė [2015;](#page-11-0) Gao et al. [2019;](#page-12-2) Ouertani et al. [2022\)](#page-14-2). Moreover, the sorption characteristics of diferent sampling positions of the same wood species and the sorption behavior between juvenile and mature wood also difer (Lenth and Kamke [2001](#page-13-3); Majka and Olek [2008;](#page-13-4) Esteban et al. [2015;](#page-12-3) Lopes et al. [2022](#page-13-5); Garcia et al. [2022\)](#page-12-4). The heartwood and sapwood in wood can also influence the sorption isotherm (Ball et al. [2001;](#page-11-1) Obataya et al. [2006;](#page-13-6) Broda et al. [2019;](#page-12-5) Quartey et al. [2021;](#page-14-3) Lopes et al. [2022](#page-13-5)). Experiments have also revealed diferences in hygroscopicity between normal and compression (tension) wood (Gorišek and Straze [2006](#page-12-6); Huda et al. [2018](#page-13-7); Zhan et al. [2021;](#page-14-4) Majka et al. [2022a](#page-13-8)). The hygroscopicity differences of samples studied above are due to variations in structure and chemical composition. Earlywood and latewood are derived from the same cambial initial cells in the cambium layer, while their cell morphology and cell wall structure difer dramatically according to the season. Earlywood cells are produced during the spring growth period and have expanded lumens and relatively thin cell walls. Latewood tracheid has smaller lumens with thicker cell walls that provide the mechanical strength to support the large tree size (Kurata et al.  $2018$ ). Therefore, theoretically, the structure and chemical composition of earlywood and latewood will be diferent, afecting their sorption properties.

As early as the 1970s, Ahlgren et al. ([1972](#page-11-2)) began to study the diferences in sorption characteristics between earlywood and latewood. The fber saturation point (FSP) was determined to be higher in earlywood than in latewood in Douglas fr (*Pseudotsuga menziesii*) and aspen (*Populus tremuloides*) by the exclusion solute method. However, due to the technical level constraints, the measured FSP was too high, and the accuracy remains to be discussed. Kärenlampi et al. [\(2005](#page-13-10)) showed that the equilibrium moisture content (EMC) of spruce latewood was slightly higher than that of earlywood, and the EMC of the two did not change after multiple moisture sorption cycles. Derome et al. ([2011](#page-12-7)) and Patera et al. [\(2013](#page-14-5)) also showed that the EMC of Norway spruce (*Picea abies*) latewood was higher than that of earlywood at the same RH, attributed to the thicker S2 layer of latewood. Their article focused on the swelling and shrinkage of wood, and did not deeply explore the sorption characteristics of earlywood and latewood. Hill et al. ([2015](#page-13-1)) used a dynamic vapor sorption (DVS) analyzer to study the sorption characteristics of earlywood and latewood in diferent annual rings of Japanese larch wood (*Larix kaempferi*), confrming the diference between the two,

showing that the hygroscopicity of earlywood was stronger than that of latewood in the same growth ring, which became more pronounced as the distance from the pith increased. In addition, the results indicated that the sorption isotherms of earlywood had good reproducibility after two sorption cycles, while the sorption isotherms of latewood showed signifcant diferences. Research by Bonnet et al. [\(2017](#page-12-1)) showed that the diference in sorption isotherms between earlywood and latewood was caused by the diference in sorption capacity, and the environment and role of bound water in earlywood and latewood was similar. However, not all studies were as speculated; that is, the sorption characteristics of earlywood and latewood were different. Neimsuwan et al. [\(2008\)](#page-13-11), Sargent et al. ([2010](#page-14-6)), Shar-ratt et al. [\(2010\)](#page-14-7) and Hill et al. [\(2011\)](#page-13-12) studied the sorption isotherms of earlywood and latewood of loblolly pine (*Pinus taeda*), radiata pine (*Pinus radiata*), Scots pine (*Pinus sylvestris*) and Sitka spruce (*Picea sitchensis*), respectively. The results indicated that the sorption isotherms of earlywood and latewood almost overlapped under any RH condition. Compared with latewood, earlywood responded more rapidly to changes in environment RH, and the sorption rate of earlywood was higher than that of latewood. Therefore, it is still controversial whether the sorption characteristics of earlywood and latewood are diferent, and further discussion and research are needed.

Desorption gives higher EMC than adsorption at equal environmental conditions, a phenomenon termed sorption hysteresis. Hysteresis can be interpreted by the 'ink-bottle' theory (McBain [1935](#page-13-13)), the hydroxyl groups concentrations participating in adsorption and desorption (Urquhart [1960](#page-14-8)), or the 'contact angle' theory (Chen and Wangaard [1968](#page-12-8)), changes in the free volume in the glassy state of the polymer (Vrentas and Vrentas [1996\)](#page-14-9) and the formation of metastable states of adsorbate in fxed pores (Sander et al. [2005\)](#page-14-10). Both the 'ink-bottle' and 'contact angle' theories assume the presence of liquid water, that is, capillary water. Based on the conceptual framework of Vrentas and Vrentas ([1996](#page-14-9)), researchers proposed that the sorption hysteresis of wood is related to changes in the softening properties of the constituent wood polymers during water vapor sorption; in other words, adsorption and desorption take place in materials with diferent physical properties (Hill et al. [2010;](#page-13-14) Engelund et al. [2013;](#page-12-9) Fredriksson and Thybring [2018;](#page-12-10) Salmén and Larsson [2018](#page-14-0)). Although the sorption hysteresis behavior of wood has been documented, the investigations on the sorption hysteresis behavior of earlywood and latewood were very limited.

The aim of this study was to investigate the sorption behavior of earlywood and latewood in the same growth ring of *C*. *bungei* and explain mechanisms in terms of their sorption behavior. Adsorption and desorption behavior of earlywood and latewood in the same growth ring of *C*. *bungei* wood samples was documented using a dynamic vapor sorption (DVS) resolution. The results were analyzed using the Guggenheim–Andersen–de Boer (GAB) model, and the sorption isotherms and hysteresis of *C*. *bungei* earlywood and latewood were compared. The efects of structure and chemical components on earlywood and latewood's sorption isotherms and hysteresis were discussed.

<span id="page-3-0"></span>

Results represent the average $\pm$ SD from three independent experiments

<span id="page-3-1"></span>**Table 2** Extract content and average hysteresis coefficient of bamboo, rattan and *C. bunget* 

References	<b>Species</b>	Extract $(\%)$ Benzene-alcohol	Average hyster- esis coefficient	
Zhang et al. $(2002)$	Bamboo	6.47	0.88	
Wu (2007)	Rattan	4.02	0.80	
	C. bungei of latewood	3.98	0.77	
	C. bungei of earlywood	2.05	0.70	

# **Materials and methods**

### **Sample preparations**

Clear wood samples without any visible defects or knots were cut from the 32nd growth ring of the heartwood of a 44-year-old *C*. *bungei* tree. The earlywood and latewood from the 32nd growth ring were used because they have representative oven-dry density. Most importantly, the 32nd growth ring is wider than other growth rings allowing obtaining an equal volume of earlywood and latewood samples. Earlywood and latewood samples were rectangular solids within 2.5 (radial) $\times$ 4 (tangential) $\times$ 4 (longitudinal) mm<sup>3</sup> dimensions. All samples were dried in a sealed container with phosphorus pentoxide at room temperature until a constant mass was achieved. The oven-dry density of earlywood and latewood was  $330 \text{ kg/m}^3$  and  $410 \text{ kg/m}^3$ , respectively. The average values of fve replicates per sample are reported.

### **Determination of chemical components**

The contents of cellulose, hemicellulose and lignin in earlywood and latewood of *C*. *bungei* were determined by Van Soest's analytical method, and the results are shown in Table [1.](#page-3-0) The Soxhlet extraction-rotary evaporation method was used to determine the benzene–alcohol extract content, and the results are shown in Table [2.](#page-3-1)

### **Dynamic water vapor sorption**

Wood samples' water vapor sorption behavior was determined using a dynamic vapor sorption apparatus (DVS Resolution, Surface Measurement Systems, UK). The samples were exposed to relative humidity (RH) variations for adsorption and desorption, as shown in Fig. [1](#page-4-0). The adsorption and desorption periods were taken at a constant temperature of  $25 \pm 0.1$  °C for approximately 9 days. Adsorption started at 0% RH and increased in 10% RH increments up to 95% RH, and desorption decreased to 0% RH, also in 10% RH decrements. Referring to the fndings of Glass et al. ([2017,](#page-12-11) [2018\)](#page-12-12), combined with the authors' previous experimental experience (Ouyang et al. [2022](#page-14-13)), samples were maintained at a constant RH, until the weight change was less than 0.002% min−1 for 10 min and then continued at the current RH for 180 min. Data on weight changes were acquired every minute.

#### **Guggenheim–Andersen–de Boer (GAB) model**

The GAB model, frequently applied to modeling the sorption isotherms of bamboo and wood (Bratasz et al. [2012](#page-12-13); Olek et al. [2013;](#page-14-14) Florisson et al. [2020](#page-12-14); Su et al. [2020](#page-14-15); Charupeng and Kunthong [2022](#page-12-15); Majka et al. [2022b\)](#page-13-15), was used to describe the water vapor sorption isotherms of earlywood and latewood samples because it is capable of describing the full shape of type II isotherm and yields meaningful physical parameters (Hartley [2000;](#page-12-16) Timmermann [2003\)](#page-14-16), and the GAB parameters can provide the internal specifc surface area of water. The GAB model is based on the theoretical concept of multilayer sorption. The model describes water molecules bonding to sorption sites to form a monomolecular layer; water molecules in the monolayer become secondary sorption sites, and additional water layers are



<span id="page-4-0"></span>**Fig. 1** Humidity conditions at each step for adsorption and desorption runs; red line represents the equilibrium stage of moisture content; blue line represents the maintenance stage of equilibrium moisture content (Colour figure online)

formed (multilayer sorption) (Basu et al. [2006\)](#page-12-17). Briefy, the model equations were as follows:

$$
EMC = \frac{100 \cdot X_{\text{m}} \cdot C \cdot K \cdot \text{RH}}{(100 - K \cdot \text{RH}) \cdot (100 + (C - 1) \cdot K \cdot \text{RH})}
$$
(1)

where EMC refers to the equilibrium moisture content of earlywood and latewood (%);  $X<sub>m</sub>$  is the monolayer capacity (%); *C* is the equilibrium constant related to the monolayer sorption; *K* is the equilibrium constant related to the multilayer sorption; and RH is the relative humidity (%). Origin 2018 (Origin Lab Corporation, Northampton, MA, USA) analysis software was used to obtain the models' parameters by the least square method and ft isothermal adsorption data.

# **Results and discussion**

#### **Adsorption and desorption isotherms**

The water vapor adsorption and desorption isotherms for earlywood and latewood samples reported as EMC against RH are depicted in Fig. [2](#page-5-0). The adsorption–desorption isotherms for all samples formed a closed loop. Meanwhile, all samples showed noticeable moisture sorption hysteresis over the full RH range. The EMC of each sample in the adsorption isotherm was lower than that in the desorption isotherm. However, the EMC values of the two sample types difer during the sorption



<span id="page-5-0"></span>**Fig. 2** Equilibrium moisture content of earlywood and latewood plotted against relative humidity during adsorption and desorption. Ad: adsorption; De: desorption

process. During adsorption (0–95% RH) or desorption (95–0% RH), the EMC of the latewood sample was higher than that of the earlywood under any RH. At the highest RH (95%), earlywood and latewood samples reached EMCs of 14.54% and 15.66%, respectively. Structurally, earlywood and latewood densities were 330 kg/  $m<sup>3</sup>$  and 480 kg/m<sup>3</sup>, respectively. On the one hand, earlywood contains a larger lumen and thinner cell wall, while latewood consists of thick-walled cells with small lumens. On the other hand, hygroscopic behavior has also shown the diference in the main components of the cell wall, as hemicelluloses provide the highest number of OH groups available for water sorption, followed by cellulose and lignin (Christensen and Kelsey [1959](#page-12-18)). It can be seen from Table [1](#page-3-0) that the content of cellulose and hemicellulose in latewood was higher than that in earlywood, and the content of lignin was lower than that in earlywood. Therefore, compared with earlywood, latewood has a higher density, higher cellulose content, higher hemicellulose content and lower lignin content, so it has more accessible OH groups (Bertaud and Holmbom [2004](#page-12-19); Bonnet et al. [2017](#page-12-1); Kurata et al. [2018\)](#page-13-9). While the large earlywood vessels commonly become embolized or occluded with tyloses by the end of the growing season in ring-porous tree species, blocking the sorption of the earlywood cell wall (Li et al. [2019](#page-13-16)). In contrast, the smaller and safer latewood vessels may remain functional for many years (Kitin and Funada [2016](#page-13-17)).

In addition, during adsorption at 80–95% RH, the sorption rate of the earlywood and latewood suddenly increased. The reason for this sudden increase in the upper end of the hygroscopic range was unknown. The diferent EMC values between earlywood and latewood under the same RH during moisture adsorption (desorption) are shown in Fig. [3.](#page-7-0) In water adsorption or desorption, the diferent EMC values between earlywood and latewood increased frst and then decreased. The turning point was 80% RH. It could be speculated that the number of micro–nano-pores in the earlywood is higher than in latewood (Engelund et al. [2013](#page-12-9)); more capillary condensed water was formed when the RH was higher than 80%, hence the phenomenon shown in Fig. [3.](#page-7-0)

#### **Sorption hysteresis**

Absolute hysteresis (obtained by subtracting the EMC of adsorption from the EMC of desorption isotherm at a constant RH) and the hysteresis coefficient (the EMC for adsorption to EMC for desorption ratio at constant RH) are two common moisture sorption hysteresis characterization methods (Olek et al. [2013](#page-14-14); Zhang et al. [2018](#page-14-17); Ouyang et al. [2022\)](#page-14-13). The changes in the absolute moisture sorption hyster-esis and moisture sorption hysteresis coefficients are shown in Fig. [4](#page-8-0). As shown in Fig. [4a](#page-8-0), the absolute hysteresis values of the earlywood and latewood samples were 1.05–2.78% and 0.92–2.56%, respectively. Regardless of earlywood or latewood, when the RH was 10–70%, the absolute hysteresis increased with the increase in RH; when the RH was 70–90%, the absolute hysteresis decreased with the increase in RH. Many previous studies (Bertolin et al. [2020;](#page-12-20) Chen et al. [2020](#page-12-0); García-Iruela et al. [2020\)](#page-12-21) had also observed this phenomenon. The absolute hysteresis of samples decreased at 70% RH, most likely due to hemicelluloses softening (Olsson and



<span id="page-7-0"></span>**Fig. 3** Diference of equilibrium moisture content for earlywood and latewood during adsorption or desorption as a function of relative humidity

Salmén [2003\)](#page-14-18). One explanation is that it crosses the glass transition point at this moisture range at room temperature, allowing the accommodation of more water molecules within the wood's cell wall (Engelund et al. [2013\)](#page-12-9). Another explanation is that when a glassy solid absorbs or desorbs water, it is afected by the "rigidity" of the macromolecules. It is likely that molecular chains cannot be quickly arranged to adapt to the entry and exit of water molecules, so the adsorption and desorption processes occur in diferent physical environments and cause hysteresis (Hill et al. [2009](#page-13-18), [2010](#page-13-14)); while RH is higher than 70%, the molecule is in a rubbery state, it is more fexible and can respond immediately to the entry and exit of water molecules. Hence, the hysteresis weakens or even disappears (Hou et al. [2022](#page-13-2)). In addition, under any RH condition, earlywood absolute hysteresis was larger than that of latewood, which is also due to earlywood lignin content being higher than that of latewood (27.38%>21.95%); higher lignin content will cause more absolute hysteresis in the wood cell wall (Hill et al. [2009;](#page-13-18) Kulasinski et al. [2015;](#page-13-19) Derome et al. [2018](#page-12-22); Yang et al. [2018\)](#page-14-19). There are many unsaturated groups in the molecular structure of lignin, reducing the lignin molecules' fexibility and increasing hyster-esis (Lu and Pignatello [2004\)](#page-13-20). Hemicellulose also affects absolute hysteresis. Zhou et al.  $(2016)$  $(2016)$  found that the higher the hemicellulose content, the greater the absolute hysteresis. According to Hou et al. [\(2022](#page-13-2)), this was because the complex network formed between hemicellulose and lignin reduces the mobility of hemicellulose; the molecular chain cannot be arranged quickly enough to adapt to the entry and exit of water molecules, showing an absolute hysteresis increase. However, Table [3](#page-9-0) shows that the lignin content of latewood was lower than in earlywood  $(21.95\% < 27.38\%)$ , while the hemicellulose content was higher than in earlywood  $(16.16\% > 12.13\%)$ .



<span id="page-8-0"></span>Fig. 4 Absolute hysteresis (a) and hysteresis coefficient (b) of earlywood and latewood samples

Moreover, from previous studies (Hill et al. [2009](#page-13-18); Kulasinski et al. [2015;](#page-13-19) Zhou et al. [2016](#page-14-20); Derome et al. [2018;](#page-12-22) Yang et al. [2018;](#page-14-19) Hou et al. [2022\)](#page-13-2), lignin and hemicellulose contents were positively correlated with the absolute hysteresis. Therefore, it is speculated that lignin has a more pronounced infuence on absolute hysteresis than hemicellulose. Furthermore, many tyloses in vessels of earlywood can also increase absolute hysteresis. The existence of many tyloses in the vessels of earlywood exerts a physical barrier effect on the moisture sorption of earlywood (Li et al. [2019\)](#page-13-16).

As shown in Fig. [4](#page-8-0)b, the hysteresis coefficient ranges of earlywood and latewood were 0.56–0.91 and 0.65–0.95, respectively. Under any RH condition, the hysteresis coefficient of latewood was larger than that of earlywood. Zhang et al.  $(2018)$  $(2018)$  calculated the hysteresis coefficient of fourteen kinds of bamboos, and the hysteresis coefficient with an average of 0.88; the average hysteresis coefficient of rattan was  $0.80$  (Yang et al.  $2021$ ). However, hysteresis coefficients in earlywood and latewood

Samples	Adsorption					Desorption			
	$X_{m}(\%)$	$\mathcal{C}_{0}^{0}$	K	$R^2$ (%)	$S_{\text{GAB}}$ (m <sup>2</sup> /g)	$X_{\rm m}(\%)$	$\mathcal{C}_{0}$	K	$R^2$ (%)
Earlywood	6.87	3.84	0.58	99.74	261	9.80	5.94	0.47	99.76
Latewood	7.47	4.46	0.60	99.81	284	11.07	5.91	0.47	99.79
Bamboo <sup>a</sup>	4.47	4.70	0.80	95.69	170	9.07	3.91	0.61	96.17
Rattan <sup>b</sup>	7.67	5.42	0.74	99.43	293	10.33	5.95	0.53	99.46
Spruce <sup>c</sup>	5.18	11.41	0.76	99.66	197				
Douglas firc	5.07	12.12	0.75	99.68	194				

<span id="page-9-0"></span>**Table 3** Fitted model parameters and internal specifc surface areas for earlywood and latewood in *Catalpa bungei*, bamboo, rattan, Spruce (*Picea abies*), and Douglas fr (*Pseudotsuga menziesii*) based on the GAB model

*X*m is the monolayer capacity (%), *C* equilibrium constant related to the monolayer sorption, *K* equilibrium constant related to the multilayer sorption,  $R^2$  coefficient of determination,  $S_{\text{GAB}}$  is the internal specifc surface area

a Zhang et al. [\(2018](#page-14-17))

 $\rm ^{b}Yang$  et al. ([2021\)](#page-14-21)

 $\mathrm{^cGao}$  et al. [\(2018](#page-12-23))

of *C*. *bungei* were 0.70 and 0.77, respectively. Compared with rattan and bamboo, hysteresis coefficient of *C. bungei* was relatively small, which might be related to its low extract content, as shown in Table [2.](#page-3-1) It is known that the presence of extractives in wood can infuence the sorption isotherm (Popper et al. [2007\)](#page-14-22). The presence of extractives clogs pores and other channels inside the material preventing the free entry and exit of water molecules (Kymäläinen et al. [2018](#page-13-21)). Therefore, the hysteresis coefficient increased. It could also be seen that the extract content of earlywood was the lowest, so its hysteresis coefficient was less than that of latewood.

The water sorption hysteresis variation of diferent samples seems to be a very complex phenomenon. Hou et al. ([2022\)](#page-13-2) showed in their research that the interaction and cross-linking between wood components infuenced hysteresis. Hence, a more detailed study is required to explain the diference in the water sorption hysteresis behavior of diferent samples.

### **Fitting the GAB model to the date**

The results of ftting the GAB model to the data of the earlywood and latewood samples are presented in Table [3.](#page-9-0) The GAB model perfectly fits the experimental data ( $R^2 \ge 99.7\%$ ) over the full RH range. The fits were valid as all the  $R^2$  values were above 99.0% (Esteban et al. [2015\)](#page-12-3). GAB parameters can be used to compare the hygroscopic properties of the earlywood and latewood samples. Among them, the  $X<sub>m</sub>$  obtained from the adsorption branch refers to the moisture content when the monolayer is full and can be used to estimate the internal specifc surface area corresponding to the monolayer capacity. The internal specific surface area  $(S<sub>GAB</sub>)$  is defned as

$$
S_{\text{GAB}} = \frac{X_{\text{m}} \cdot \rho \cdot N_{\text{A}} \cdot \sigma}{M} \tag{2}
$$

where  $\rho$  is water density;  $N_A$  is the Avogadro number,  $6.022 \times 10^{23}$ ;  $\sigma$  is the average area where water occupies the complete monolayer  $(0.114 \text{ nm}^2 \text{ was used in this})$ study), and *M* is the molar mass of water, 18 g/mol. As shown in Table [3,](#page-9-0)  $X<sub>m</sub>$  of earlywood and latewood samples is 6.87% and 7.47% for adsorption, respectively. Correspondingly,  $S_{\text{GAB}}$  of the two is 261 m<sup>2</sup>/g and 284 m<sup>2</sup>/g, respectively. Both  $X_{\text{m}}$  and  $S<sub>GAB</sub>$  are higher in the latewood samples than in the earlywood samples, corresponding to the greater cellulose and hemicellulose content in latewood than in earlywood (Table [1](#page-3-0)), indicating that both the hydrophilic group content and the monolayer adsorption capacity are greater in the latewood than in the earlywood. As shown in Table [3](#page-9-0),  $X_m$  and  $S_{\text{GAB}}$  of the earlywood and latewood of the hardwood *C. bungei* are similar to those of rattan and higher than bamboo and some softwoods, indicating that their hydrophilic group content is greater than that of bamboo and some softwoods. The  $X<sub>m</sub>$  values were consistently lower for adsorption than desorption processes (Olek et al. [2013](#page-14-14); Majka et al. [2022b\)](#page-13-15). This is consistent with the results reported by Krupińska et al. ([2007\)](#page-13-22) and indicates that during adsorption, the binding energy between the active sites and multilayer water molecules is higher than during desorption.

The values of the *C* in Table [3](#page-9-0) are higher than 2 for earlywood and latewood samples. Therefore, the necessary condition for classifying the isotherms as type II was satisfed (Olek et al. [2013](#page-14-14); Majka et al. [2022b](#page-13-15)). Lewicki ([1997\)](#page-13-23) states that type II isotherms should also satisfy the following two inequalities, where 5.57≤*C*<∞ and 0.24<*K*≤1. These additional conditions were met for desorption isotherms only. That means, the adsorption isotherms cannot be fully classifed as type II. Except for bamboo, higher *C* values were noticed during desorption than adsorption (Table [3\)](#page-9-0). Hess et al. [\(2018\)](#page-13-24) attributed diferences in *C* values for desorption and adsorption to sorption hysteresis. The additional thermodynamic analysis of the GAB model was made by Pradas et al. ([2004\)](#page-14-23), and the so-called jamming phenomenon was found. The phenomenon was related to forming the frst layer of the adsorbed water. It was indicated that not all sorption sites were occupied during adsorption, not even at saturation. The sufficient condition for the jamming phenomenon was given by the relation *K* (equilibrium constant related to the multilayer sorption  $\leq 1$ . The fraction of the total number of sorption sites occupied at saturation *f* was defned as:

$$
f = \frac{K \cdot C}{K \cdot C + (1 - K)}
$$
(3)

For all adsorption processes analyzed in the present study, *K* was always lower than 1 (Table [3](#page-9-0)). The *f* for earlywood and latewood was 0.84 and 0.86, respectively, i.e., the proportion of the total number of sorption sites occupied by latewood samples in the saturated state was high. The observed values of *C* were always signifcantly higher than *K* in corresponding isotherms (Table [3](#page-9-0)). This suggests that monolayer water molecules might be much stronger bound than those with multilayer bonding (Hess et al. [2018](#page-13-24)).

# **Conclusion**

The following conclusions could be drawn from the sorption isotherm behavior of homogenous catalpa wood samples documented by DVS Resolution:

- (1) During adsorption or desorption, the EMC of latewood was higher than in earlywood under any RH: meanwhile, the EMC diference between earlywood and latewood increased frst and then decreased, and the turning point was 80% RH, related to the diferent number of micro–nano-pores in earlywood and latewood.
- (2) Adsorption–desorption isotherms formed a closed loop, all samples showed noticeable water sorption hysteresis over the full RH range, and the absolute hysteresis increased and then decreased due to hemicelluloses softening, with an infection point at 70% RH. The absolute hysteresis of earlywood was larger than that of latewood, while its hysteresis coefficient was smaller, related to the diferences in structure and chemical composition.
- (3) The GAB model could predict the sorption isotherms of earlywood and latewood. The  $X<sub>m</sub>$  for earlywood and latewood was 6.87% and 7.47%, respectively. In particular, the GAB model confirmed more  $S_{\text{GAB}}$  in latewood than in earlywood, indicating greater hydrophilic group content and monolayer adsorption capacity in latewood than in earlywood. The adsorption isotherms of earlywood and latewood in *C*. *bungei* cannot be fully classifed as type II. The *f* for earlywood and latewood was 0.84 and 0.86, respectively, i.e., the proportion of the total number of sorption sites occupied by latewood samples in the saturated state was high.

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# **Declarations**

**Confict of interest** The authors declare no competing interests.

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