THE KINETICS OF WATER VAPOUR SORPTION: ANALYSIS USING PARALLEL EXPONENTIAL KINETICS MODEL ON SIX MALAYSIAN HARDWOODS

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ZAIHAN J, HILL CAS, CURLING S, HASHIM WS & HAMDAN H. 2010. The kinetics of water vapour sorption: analysis using parallel exponential kinetics model on six Malaysian hardwoods. Six Malaysian hardwoods, chengal (*Neobalanocarpus heimii*), kapur (*Dryobalanops* spp.), keruing (*Dipterocarpus* spp.), ramin (*Gonystylus* spp.), acacia (*Acacia mangium*) and sesendok (*Endospermum malaccense*) were studied to determine their sorption kinetics behaviour using a dynamic vapour sorption (DVS) apparatus. Experimental data fitted well to the parallel exponential kinetics (PEK) model. The PEK model expresses the sorption kinetics as fast and slow sorption processes, but interpretation of how these can be related to physical phenomena is not yet understood. The Hailwood–Horrobin model was also used to examine the relationship between sorbed monolayer water and polylayer water at different relative humidities. Comparison between the two models was used to verify if the fast and slow sorption processes could be linked to monolayer or polylayer water formation in the cell wall. Characteristic times at various relative humidities showed differences between adsorption and desorption in the slow process for all the species. However, using mass change criterion, sorption hysteresis was found to occur in both the slow and fast processes.

Keywords: Sorption kinetics, isotherm, hysteresis, dynamic vapour sorption, tropical

ZAIHAN J, HILL CAS, CURLING S, HASHIM WS & HAMDAN H. 2010. Kinetik erapan wap air: analisis menggunakan model kinetik eksponen selari terhadap enam kayu keras Malaysia. Enam kayu keras Malaysia iaitu chengal (*Neobalanocarpus heimii*), kapur (*Dryobalanops* spp.), keruing (*Dipterocarpus* spp.), ramin (*Gonystylus* spp.), acacia (*Acacia mangium*) dan sesendok (*Endospermum malaccense*) dikaji untuk menentukan perilaku kinetik erapan menggunakan alat erapan wap dinamik (DVS). Data dianalisis menggunakan model kinetik eksponen selari (PEK) dan didapati padan dengan data eksperimen. Model PEK menerangkan pembahagian lengkungan kinetik erapan kepada proses cepat dan proses lambat. Namun tafsiran bagaimana proses-proses cepat dan lambat boleh dikaitkan dengan fenomena fizikal masih belum difahami. Model Hailwood–Horrobin juga digunakan untuk meneliti hubungan antara air lapisan mono dan air lapisan poli pada kelembapan relatif yang berbeza. Perbandingan dua model ini digunakan untuk mengesahkan jika proses cepat dan lambat dapat dikaitkan dengan pembentukan lapisan air mono dan air poli di dalam dinding sel. Ciri masa pada kelembapan relatif yang berbeza menunjukkan bahawa perbezaan antara penjerapan dan penyaherapan berlaku hanya dalam proses lambat bagi setiap spesies. Bagaimanapun, dalam penggunaan kriteria perubahan berat, histeresis erapan berlaku dalam kedua-dua proses cepat dan lambat.

INTRODUCTION

One of the important factors affecting the equilibrium moisture content (EMC) of wood is the relative humidity (RH) to which the material is exposed. Wood adsorbs moisture when transferred from low to high humidity environments and desorbs moisture when transferred from high to low humidity. The sigmoid curve relating EMC and RH at constant temperature is called a sorption isotherm. Most studies on the sorption isotherm characteristics of wood have until recently used saturated salt solutions. The dynamic vapour sorption (DVS) apparatus is a relatively new equipment developed to measure continuous weight change over time at relative humidities (RH) between 0 and 95% within a short period of time (Hill *et al.* 2009, Zaihan *et al.* 2009). DVS has the advantage of determining the rate of change of

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the sample mass over time as the sample adsorbs or desorbs moisture as it approaches equilibrium. Determining the EMC of wood at a given RH is a means of evaluating sorption properties of wood.

The DVS moisture sorption isotherm data can also be used as inputs for sorption kinetics studies. In natural fibres and foodstuffs, the parallel exponential kinetics (PEK) model has been found to give exceptionally good fits to both the adsorption and desorption data. Kohler *et al.* (2003) found that the PEK model produced an excellent fit to the experimental sorption and desorption curves as the sample (flax fibre) approached equilibrium. This shows the existence of two distinct mechanisms for the exchange of water vapour. The two mechanisms—fast and slow processes—are attributed to different sorption sites. However, there is at present no consensus as to what these two processes represent physically (Kohler *et al.* 2003, Okubayashi *et al.* 2004, Kachrimanis *et al.* 2006, Kohler *et al.* 2006).

In this study the Hailwood–Horrobin (HH) (Hailwood & Horrobin 1946) and PEK models were used to analyse the sorption isotherms and sorption kinetics of the wood. The comparison between the PEK model and the HH model was used to determine if there was a relation between the PEK fast and slow processes and the formation of HH monolayer and polylayer water. There is very little data in the literature for proper assessment of what variables may affect the kinetics. Variation of wood cell wall composition may have an effect on the sorption process and provides insights into the PEK model and possibly the phenomenon of hysteresis. Although there are many studies on water vapour sorption of wood, there are relatively few on tropical hardwoods. The main objective of this study was to establish the dynamic water sorption properties of Malaysian hardwood using dynamic vapour sorption (DVS) apparatus.

MATERIALS AND METHODS

Sample preparation

Six wood species, chengal (*Neobalanocarpus heimii*), kapur (*Dryobalanops* spp.), keruing (*Dipterocarpus* spp.), ramin (*Gonystylus* spp.), acacia (*Acacia mangium*) and sesendok (*Endospermum malaccense*) were used in this study. All the samples were kiln dried and obtained from the Forest Research Institute Malaysia. The wood samples were ground to fine particles and passed through a BS410-1:2000 mesh sieve no. 20 (0.841 mm sieve opening).

Determination of extractive content

Extractive analysis was carried out on air-dried wood meal, which was passed through a BS 60 mesh sieve (250 μm). The method used was ethanol–toluene solubility according to the TAPPI test method 204 cm-93 (TAPPI 1994).

Determination of sorption isotherm data using DVS intrinsic apparatus

Isotherm analyses were performed using DVS intrinsic apparatus. The DVS is designed to accurately measure the change in mass of a sample as it sits in an atmosphere of precisely controlled concentrations of water vapour in a stream of nitrogen carrier gas. The sample was placed onto a clean sample pan which was carefully placed on the hang down wire connected to the microbalance. Then the sample chamber was closed. Nitrogen gas with a pre-set percentage RH was passed over the sample at a flow rate of 200 $cm^3 s^{-1}$ and at a temperature of 25.0 ± 0.1 °C. The sample mass readings from the microbalance reveal the vapour adsorption/desorption behaviour of the sample. The schedule for the DVS was set to 14 different RHs (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 85, 90 and 95%). Data on mass change were acquired every 20 s. The instrument maintains a constant target RH whereby the moisture content change of sample per minute (dm/dt) is less than 0.0002% min^{-1} over a 10 min period. Humidity and temperature probes were located in close proximity to the sample and reference holders providing direct measurement of these parameters. It was found that the temperature and humidity values were very stable during the tests, although both the RH and temperature were seldom exactly at the pre-set values and it was necessary to read the actual RH and temperature values at each adsorption and desorption stage from the output data spreadsheets.

Evaluation of sorption isotherms

Hailwood–Horrobin model

The adsorption behaviour of wood at each RH was analysed by fitting the experimental data using the HH model (Hill *et al.* 2009, Zaihan *et al.* 2009).

Parallel exponential kinetics model

Non-linear curve fitting with the function 'expassoc' (equation 1) was fitted to the adsorption and desorption data curve of the wood specimens using Origin 6.1 software (Origin Lab. Corporation USA). The PEK equation is a double exponential of the form:

$$MC = MC_0 + MC_1(1 - \exp(-(t/t_1)) + MC_2(1 - \exp(-(t/t_2)) \quad (1)$$

where MC is the moisture content at infinite time of exposure of the sample at a constant RH and MC_0 is the moisture content of the sample at time zero. The sorption kinetics curve is composed of two exponential terms which represent fast and slow processes having characteristic times of t_1 and t_2 respectively. MC_1 and MC_2 are associated moisture contents.

RESULTS AND DISCUSSION

Comparison of sorption isotherm of different fibres

All the wood species showed the classic Type II sigmoidal adsorption and desorption isotherms (Figure 1). However, there were differences in the total amount of moisture content present in the samples at higher RH values. There was little difference in MC at the range between 0 and 60% RH, but when the RH increased above 60%, each of the species started to behave differently. At the targeted 95% RH, ramin had the highest MC, followed by sesendok, kapur, keruing, acacia and chengal (Table 1). There was weak correlation between MC and extractives. Timber species with high content of extractives have been reported to exhibit lower MC (Wangaard & Granados 1967, Chong & Achmadi 1991). However, this study showed no correlation between MC and the cell wall macromolecular composition.

Sorption kinetics curve fitting

Studies using DVS determine the actual EMC in real time under set temperature and RH conditions. When the ambient RH is increased, the EMC of the wood will increase in response. Figure 2 shows the step by step increase of RH

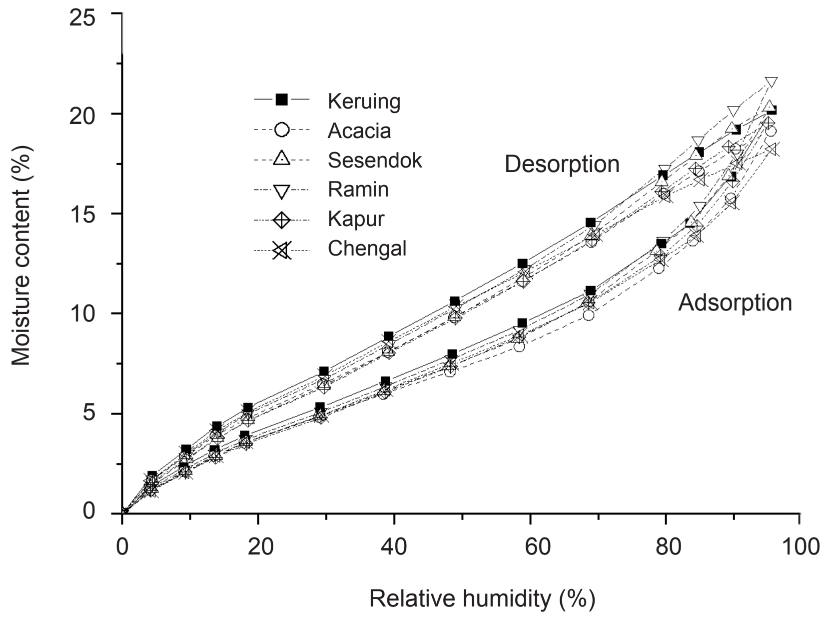

Figure 1 Experimental isotherms for adsorption and desorption for the six Malaysian hardwoods

Table 1 Moisture content at 95% RH and the chemical composition of six Malaysian hardwoods

Wood	Moisture content at 95% RH (%)	Cellulose (%)	Pentosan (%)	Lignin (%)	Extractives (%)
Chengal	18.2	49.1[a]	13.7[a]	33.4[a]	13.4
Kapur	20.2	49.5[b]	12.3[b]	32.5[b]	2.6
Keruing	19.5	52.6[c]	23.8[c]	23.8[c]	1.7
Ramin	21.6	na	na	na	1.5
Acacia	19.1	50.3[e]	18.0[e]	23.5[e]	8.1
Sesendok	20.3	42.2[d]	14.2[d]	26.3[d]	1.5

[a,b] Peel & Bhaskaran (1957), [c]Peh *et al.* (1986), [d]Rushdan *et al.* (2007), [e]Mohd Nor (1991); na = not available

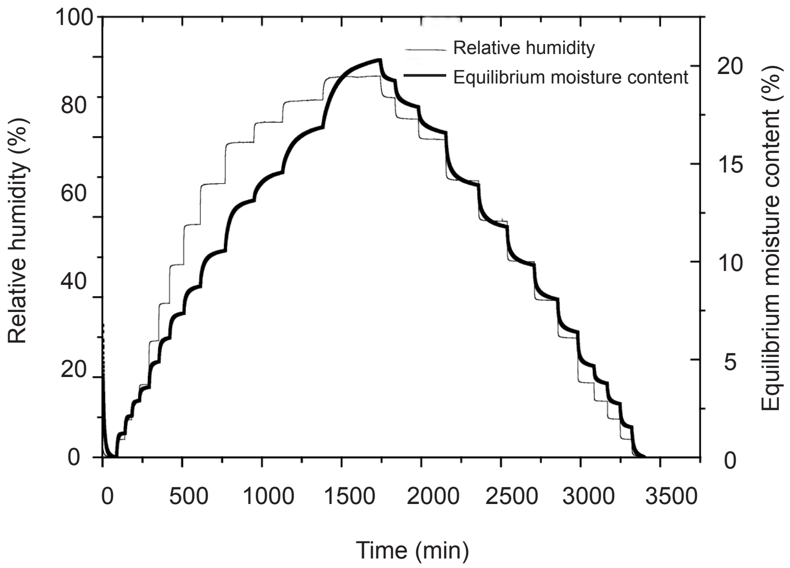

Figure 2 Adsorption and desorption curves of sesendok for one cycle. The initial decrease in moisture content is due to the drying curve of the sample in the apparatus.

and the related EMC attained by sesendok. A typical adsorption graph is shown in Figure 3 for sesendok at 25 °C. This figure shows the response of sesendok to an increase in RH from 0 to 9.3% and subsequently from 9.3 to 18.3%. The result is an asymptotic curve approaching the EMC value at infinite time of exposure at a specific RH. In an experimental sorption test, when the RH is varied, it does not change instantaneously from one value to the next and as a consequence, the response of the material is also not immediate, resulting in a transition time which can last for a few minutes. This has consequences when attempts are made to fit theoretical kinetic function to the data points.

An example of this is shown in Figures 4a and b. In Figure 4a, all the data points were included and the non-linear expassoc curve fit was applied to these data. None of the parameters were fixed and the software was allowed to iterate to the best fit. The values MC_2 and t_2 had exceedingly high errors associated with them and hence this fit was rejected. The first data point was then removed and this whole procedure was repeated until the errors associated with the parameters were acceptably low. In a sensitivity analysis, it is found that once a 'good' fit of this type is obtained, the values t_1 and t_2 become stable. However, the consequence of removing the earlier data points is that MC_1 and MC_2 give less accurate values. In Figure 4b, two data points (20, 40 s) were removed and an acceptable fit was obtained. The sum (MC_o + MC_1 + MC_2) gave the MC of the sample at infinite time of exposure to the set RH.

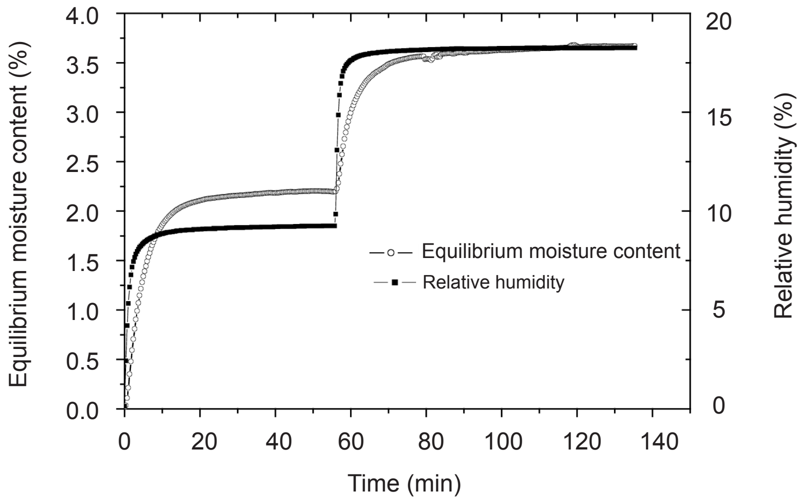

Figure 3 Adsorption kinetics curve of sesendok showing the change in sample moisture content and relative humidity against time

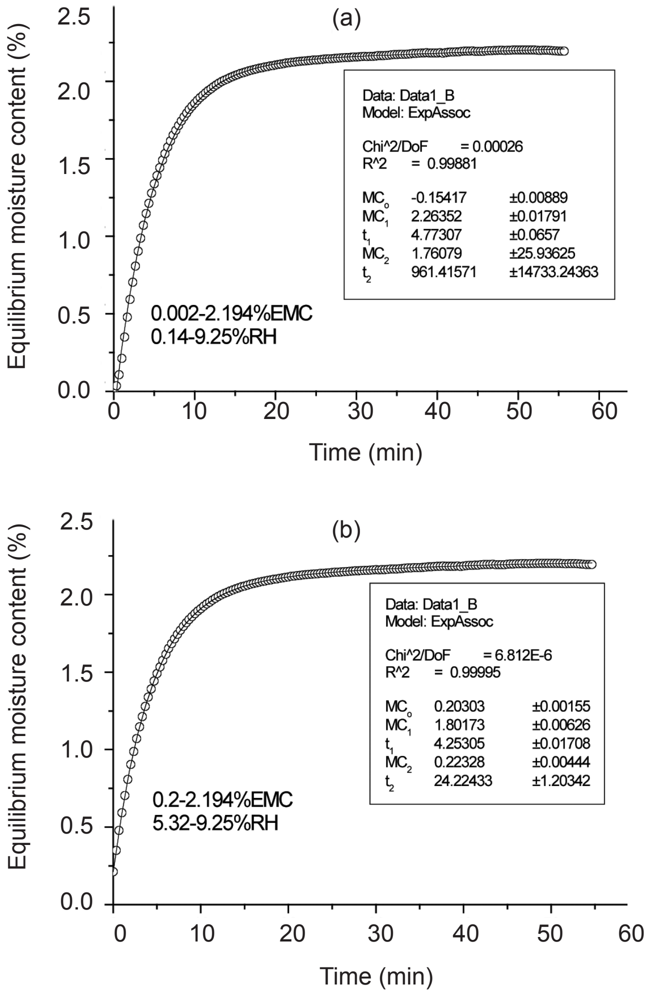

Figure 4 Non-linear curve fit to adsorption data (25 °C) for sesendok exposed to a change in relative humidity from zero to 9.25%. Inclusion of all the data points compromises the curve fit and results in inaccurate values of the characteristic times of the fast (t_1) and slow (t_2) adsorption processes (a). In (b) the first few data points have been removed resulting in a better curve fit, but now the moisture content values MC_1 and MC_2 are less accurate.

Fitting of experimental and model isotherm

The sum $MC_0 + MC_1 + MC_2$ gives an extrapolated EMC at infinite time and this can be compared with the experimental EMC as shown in Figure 5. There were good relationships between the experimentally determined and mathematically fitted isotherms. All the six Malaysian hardwoods showed good graphical fits between the experimental and calculated data.

Modelling of the sorption isotherms

As previously noted, Kohler *et al.* (2003) attributed the fast and slow processes to corresponding sites with no further attempt at interpretation, although it was suggested that this might be related to monolayer and polylayer water formation in the cell wall. In order to test this hypothesis, a comparison was made between the cumulative mass changes associated with the slow and fast processes at various RH values and the theoretical monolayer and polylayer cell wall water contents calculated from the HH model. The result of this analysis is shown in Figure 6. There was no correlation between the two kinetic processes and monolayer as well as polylayer water formation in any species.

What is the physical interpretation of the PEK model?

The PEK parameters for percentage moisture content mass changes, MC_1 and MC_2, were obtained from the DVS data for each relative humidity interval. In order to analyse the effect of the humidity on the moisture sorption behaviour in more detail, the PEK parameters for characteristic times (t_1 and t_2) at each sorption step were plotted against RH (Figure 7). It should be noted that the characteristic times in the sorption process are influenced by both the sample mass and the magnitude of change in cell wall moisture content associated with that sorption step. In adsorption, from 0 to 50% RH, the t_1 and t_2 values remained almost constant but after approximately 50% RH, both t_1 and t_2 started to increase, indicating that the equilibration process is slowing down. In desorption, the same trend is shown in all wood species. An important observation is the difference in the characteristic times between the slow adsorption and slow desorption processes, whereas there is no difference in the characteristic times of the fast processes under adsorption and desorption conditions.

The time to equilibrium was always longer for the slow desorption process, which shows that there is a lack of symmetry between the adsorption and desorption that most probably has its origin in the micromechanical behaviour of the cell wall in the presence of moisture. Above 80% RH, the characteristic time increased greatly in all the woods studied, especially during adsorption. At 0% RH, during desorption, sesendok had the highest equilibration time compared with the other wood species.

Hysteresis effect of the fast and slow kinetic mass components

The fast process is related to the characteristic time t_1 and the moisture content at infinite time MC_1 and the slow process, to the values t_2 and MC_2. In the desorption process for the kinetic curve, the MC_1 and MC_2 values were negative. The cell wall moisture content associated with the slow and fast kinetics showed hysteresis between the adsorption and desorption cycle. Figure 8 shows that different species show different sorption hysteresis behaviour. Chengal, ramin and acacia exhibited larger hysteresis in the fast process compared with the slow process. Sesendok, kapur and keruing had similar levels of hysteresis in both the slow and fast kinetic processes. This was in contrast with the case when analysing characteristic times, where differences between adsorption and desorption were found only with the slow process.

CONCLUSIONS

This study showed that there were differences in the adsorption/desorption behaviour of six Malaysian hardwoods. Analysis of sorption kinetics was conducted using the parallel exponential kinetics model, with excellent fits to the experimental data obtained. No relationship was found between the fast and slow kinetic processes and the formation of monolayer water or polylayer water at various relative humidities. This sorption kinetics study also found conflicting evidence regarding hysteresis effects of the fast and slow processes. The characteristic time criteria showed that differences between adsorption and desorption occurred only in the slow process, but when using mass change criterion, hysteresis

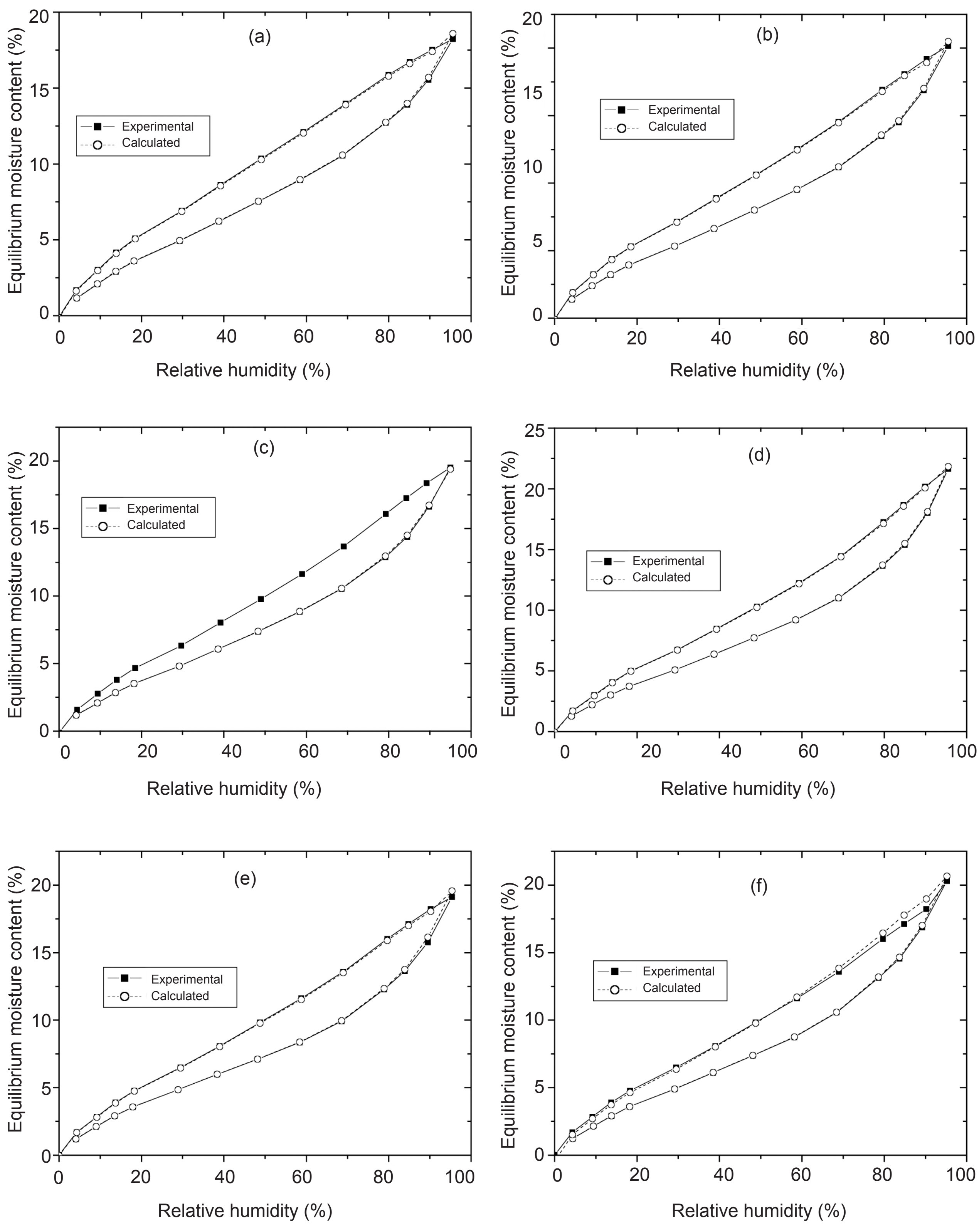

Figure 5 Comparison of isotherms derived from experimental data (filled squares) and from sums of the cumulative moisture contents of the fast and slow kinetic processes (open circle) in Malaysian hardwoods: (a) chengal, (b) kapur, (c) keruing, (d) ramin, (e) acacia and (f) sesendok

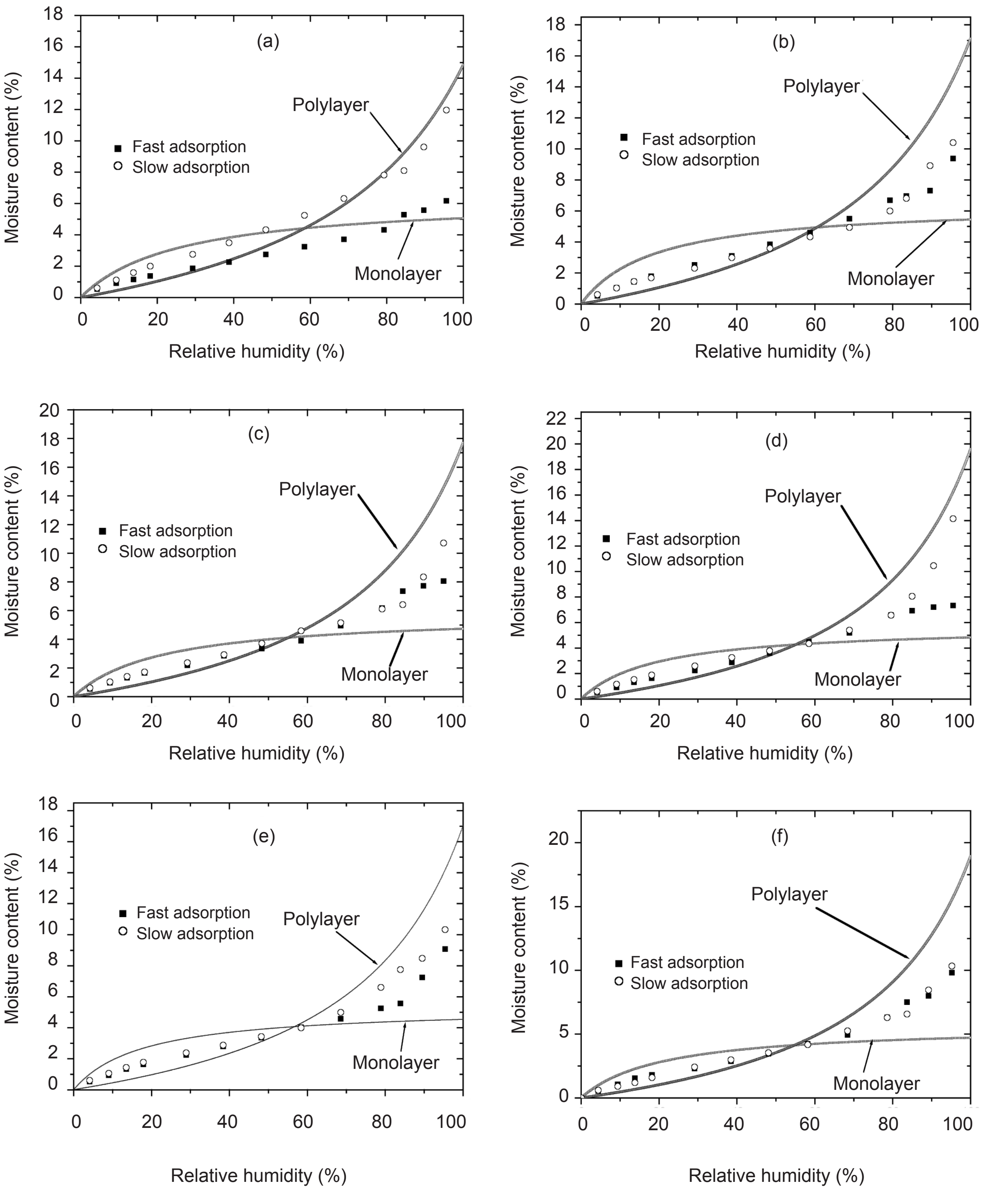

Figure 6 A comparison of the cumulative moisture contents associated with the PEK model fast and slow processes in Malaysian hardwoods: (a) chengal, (b) kapur, (c) keruing, (d) ramin, (e) acacia and (f) sesendok compared with the polylayer and monolayer curves calculated using the Hailwood–Horrobin model

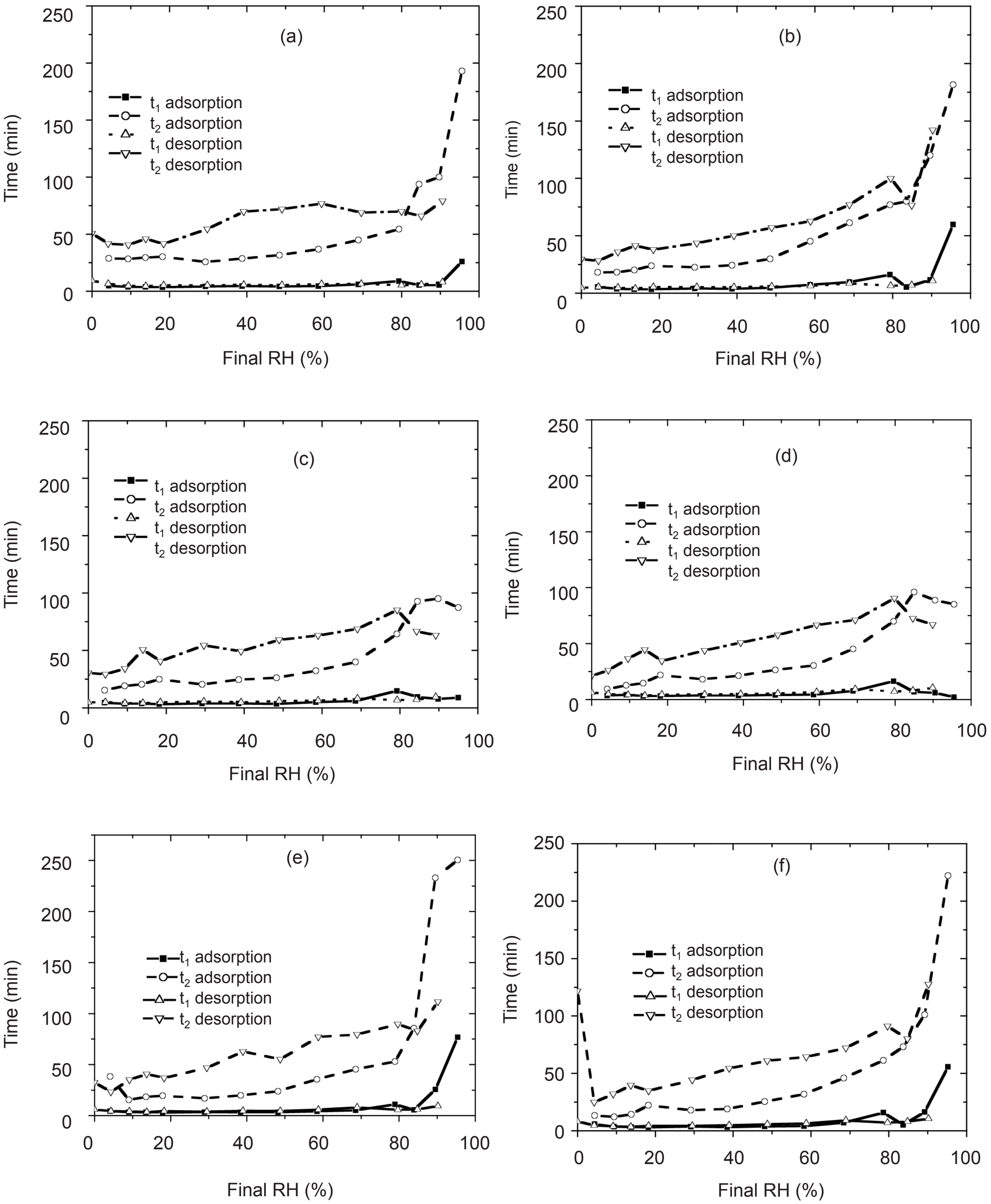

Figure 7 Variation of characteristic times with change in relative humidity for the fast (t_1) and slow (t_2) exponential kinetic processes for adsorption and desorption in Malaysian hardwoods: (a) chengal, (b) kapur, (c) keruing, (d) ramin, (e) acacia and (f) sesendok

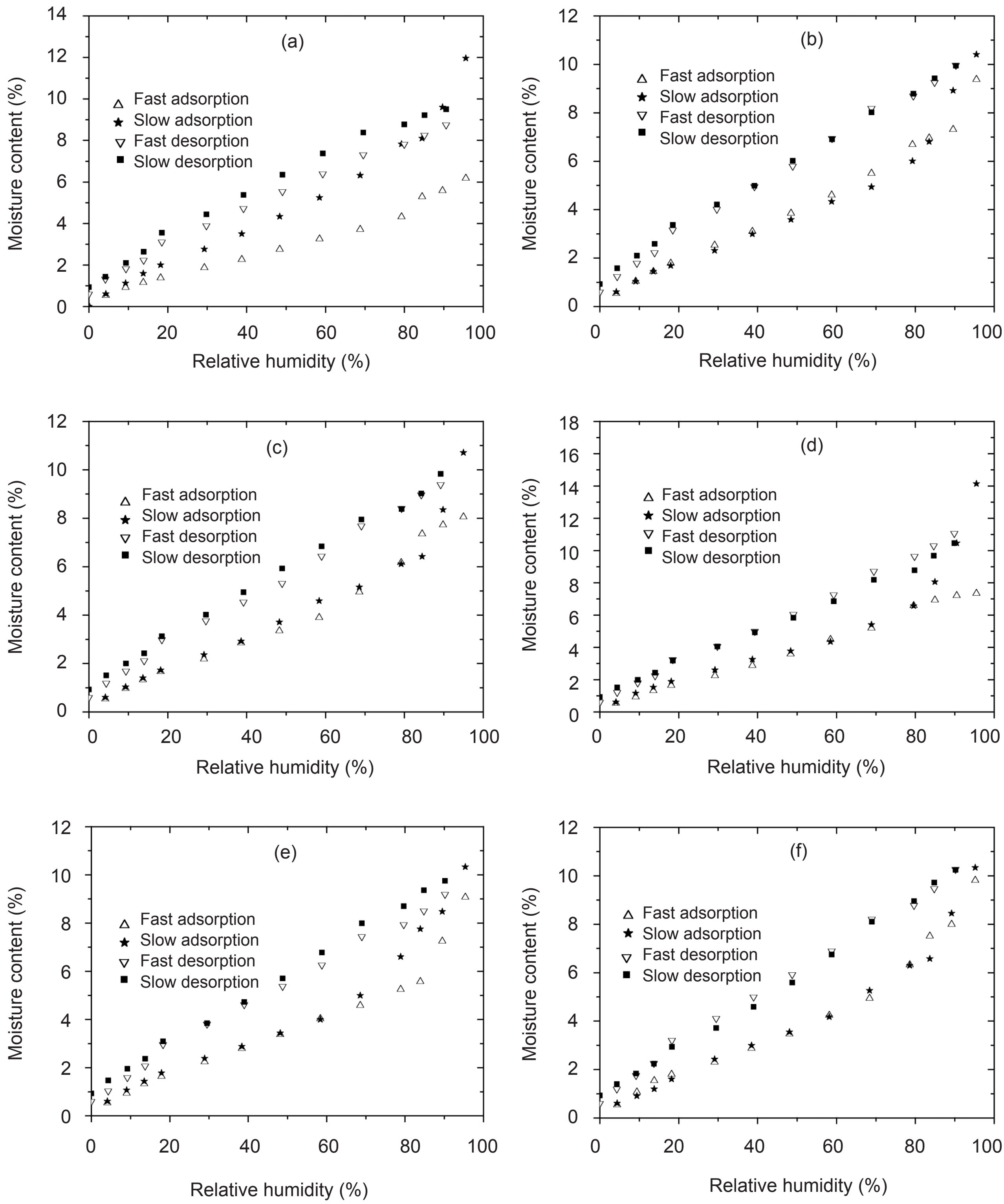

Figure 8 A comparison of the cumulative moisture contents associated with the fast and slow adsorption and desorption kinetic processes in Malaysian hardwoods: (a) chengal, (b) kapur, (c) keruing, (d) ramin, (e) acacia and (f) sesendok

occurred in both the fast and slow processes. This study shows that the parallel exponential kinetics model is most appropriate for studying cell wall sorption phenomena.

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