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ORIGINAL ARTICLE

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Water adsorption process of bamboo heated at low temperature

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Abstract Water adsorption capacities were evaluated for moso bamboo samples that were heated at 200°C for various times and conditioned in a closed container at 97% relative humidity at 20°C. Logistic regression analysis was used for curve fitting to the adsorption data and its parameters were analyzed. These parameters were compared with those derived previously from the Dubinin and Radushkevich theory. The properties of the heat-treated samples changed after 5 h of heating. With less than 5 h of heating, hydroxyl groups provided the main adsorption sites but their numbers decreased on heating. After 5 h, gasification of the bamboo increased and capillaries formed.

Key words Water adsorption · Adsorption process · Heated bamboo · Logistic regression analysis · Dubinin and Radushkevich theory

Introduction

Like wood, bamboo is a component of the forest biomass. However, the industrial potential of this resource has not been studied in depth. The properties of bamboo can be changed by heat treatment, and it is well known that both heat-treated wood and bamboo provide useful adsorbents as used in humidity conditioning.[1–6] The changes in the ultrastructure of bamboo upon heating are not well understood, but important changes occur in the water adsorption capacity of bamboo with increases in the time of heat treatment. The mechanism of these changes in adsorption properties can be examined using samples subjected to only mild heating. An understanding of the ultrastructural changes involved may facilitate exploitation of this little-used portion of the forest biomass.

We examined the water adsorption capacity of bamboo samples heated at 200°C, which is a relatively low temperature for heat treatment. The results obtained with different heating time were presented in our previous report where we examined the changes in water adsorption by analyzing the isothermal responses of different samples.[6] In the present study, the adsorption processes of these samples were examined. The samples were conditioned at 20°C under conditions of 97% relative humidity (RH), and their moisture contents were measured over time. Logistic regression analysis was applied to the results, and equation parameters were analyzed and compared with those derived from the Dubinin and Radushkevich theory.

Experimental

The same samples of 6-year-old moso bamboo (*Phyllostachys pubescens*; harvested in October 2004 in Shimane Prefecture, Japan) as used in our earlier study[6] were used here. The bamboo culm consisted of 27 internodes designated No. 1 to 27 starting from the bottom to the top of the culm. Block samples were prepared from the center of internodes No. 14 and 15 from the middle of the culm. Each block had rectangular dimensions of 20 (L) × 5 (R) × 5 (T) mm.

The samples were dried at 105°C for 24 h prior to heat treatment and then heated at 200°C for 0 h (untreated sample used as a control), 1 h (ln1 = 0), 2 h (ln2 = 0.69), 3 h (ln3 = 1.10), 5 h (ln5 = 1.61), 20 h (ln20 = 3.00), 48 h (ln48 = 3.88), 72 h (ln72 = 4.28), 120 h (ln120 = 4.79), 240 h (ln240

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= 5.48), or 360 h (ln360 = 5.89). Heating times were determined to allow the 11 data points to be plotted at near-regular intervals on a logarithmic scale. Weight loss due to heat treatment was estimated by reference to the weight of the unheated weight dried at 105°C.

Samples were placed in a desiccator with a saturated solution of K_2SO_4 to provide 97% RH and their weights were measured at 20°C for the duration of the experiment. The weight of each sample was plotted against adsorption time on a logarithmic scale. The adsorption data obtained were then analyzed using logistic regression analysis to extract the descriptive parameters.

Results and discussion

Regression curves of adsorption process

The results of adsorption by the heat-treated bamboo are shown in Fig. 1. Regression curves obtained through fitting a logistic equation to the data are shown as solid lines. All the regression curves showed excellent agreement with the observed absorption data values, lending support to the efficacy of the logistic equation to model the adsorption process of the bamboo samples. The values given by the regression curve were close to experimental data for each heat-treated sample, stabilized under the same isothermal experimental conditions.

The logistic equation used is the solution of the nonlinear differential equation as follows:

$$\frac{dy}{dx} = \frac{a}{b} y(b - y) \qquad (y = mc, x = \ln[t]) \tag{1}$$

This equation may be transformed into:

$$\frac{dy}{dx} = -\frac{a}{b}\left(y - \frac{b}{2}\right)^2 + \frac{ab}{4}. \tag{2}$$

The maximum value of adsorption rate dy/dx was then given by $ab/4$ and the solution of Eq. 1 was:

$$y = \frac{b}{1 + c\exp[-ax]} \tag{3}$$

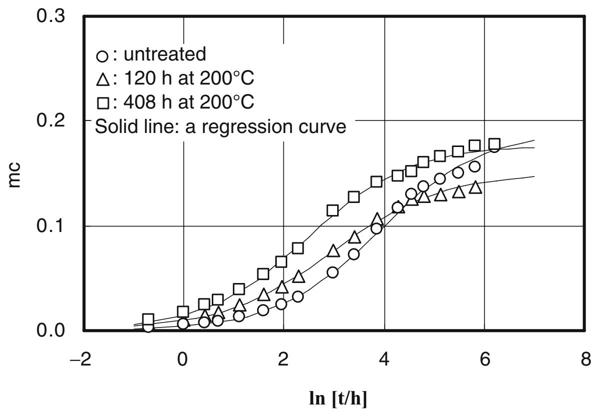

Fig. 1. Experimental data and relevant regression curves for samples heated

Equation 3 can be transformed into $1/y = (1/b) + (c/b)\exp[-ax]$, so parameters a, b, and c may be determined easily. These parameters characterize the curves in the absorption process described by Eq. 3. For an equilibrium moisture content, b denotes the value when the curve is stabilized (equilibrium moisture content), $ab/4$ is the maximum adsorption rate, and $\ln[c]/a$ is the time required to achieve this maximum adsorption rate. Hence, water adsorption in bamboo can be described by the leveling-off value b when the regression curve is stabilized, ab the maximum adsorption rate, and $\ln[c]/a$ the time taken to achieve this maximum adsorption rate. Variations in these parameters enable characterization of the differences in the adsorption process resulting from different heating times.

It should be noted that these parameters do not correspond directly to physical properties of each heated sample. Rather, the parameters describe the character of the adsorption process for each sample. Because the parameters do not relate directly to structural changes in the bamboo or other physical factors resulting from heat treatment, other considerations are needed to account for the behavior of parameters in the adsorption process.

The logistic curves derived from the observed values of each heat-treated sample and the corresponding differential curves are shown in Fig. 2. The differential curves are normalized to make the maximum rate of adsorption equal to unity. The logistic curves shown in Fig. 2 suggest that they may be placed into two groups: those heated for less than

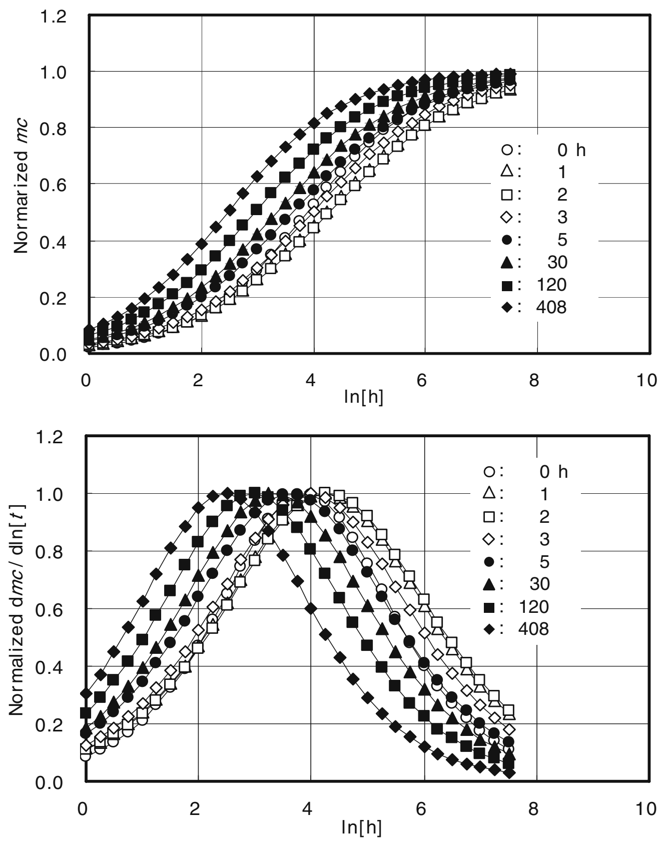

Fig. 2. Regression curves and their normalized differential curves for samples heated for 0 to 408 h

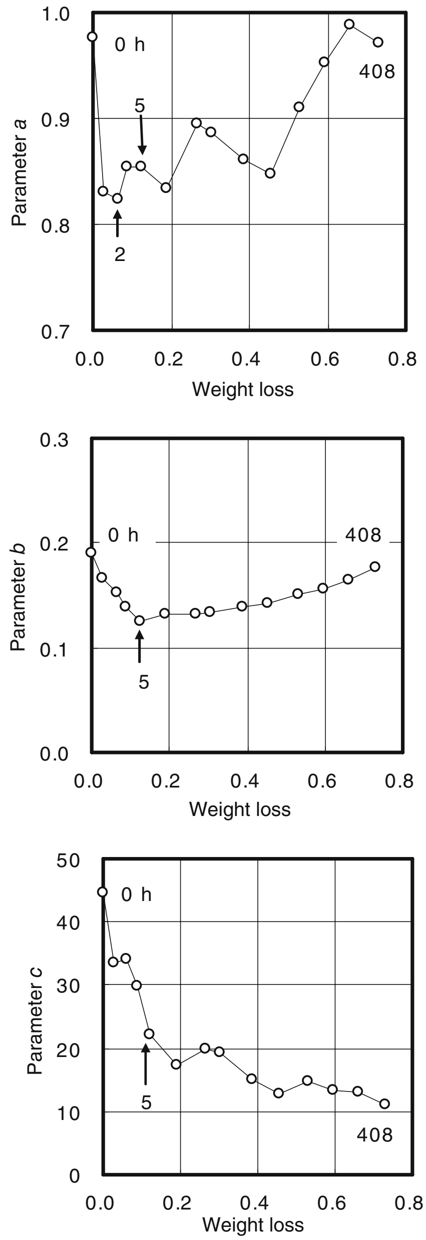

Fig. 3. Weight loss dependence of the parameters *a* (*top*), *b* (*middle*), and *c* (*bottom*) of regression curves derived from the logistic function $f(x) = b/(c + \exp[-ax])$, where $f(x) = mc$ and $x = \ln[t]$. *Numbers* on the plot indicate the heating time

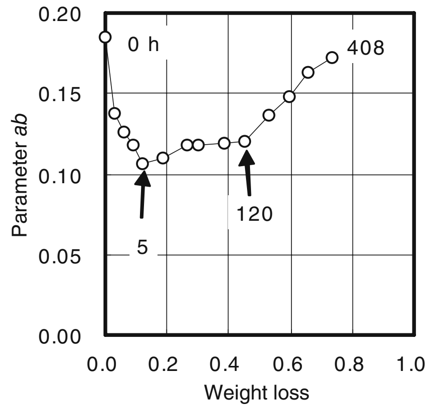

Fig. 4. Relationship between *ab* (describing the maximum adsorption rate) and weight loss

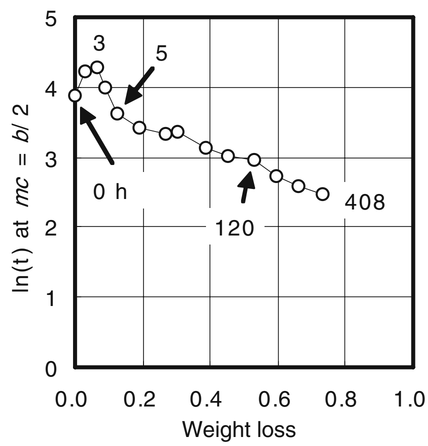

Fig. 5. Relationship between the time to achieve maximum adsorption rate, ln[*t*], and weight loss

3–5 h and those heated for more than 5 h. The differential curves lend support to this notion and show that the peak corresponding to the maximum rate of adsorption shifts to shorter time for samples heated for more than 3–5 h.

Dependence of parameters on heating time

Figure 3 shows the relationships between parameters *a*, *b*, and *c* and weight loss. An inflexion point occurred upon heating for 3–5 h. This point corresponds with that found from analysis of isotherms, as reported in our previous article.[6]

The behavior of the equilibrium moisture content, denoted here by *b*, was reported elsewhere.[6] In this previous study, we showed that a plot of equilibrium moisture content against heating time causes the minimum peak after heating for 2–5 h as a result of changes in both the chemical and physical structure. Two parameters are used to describe the adsorption curves, *ab* and ln[*t*].

Figure 4 shows *ab* against weight loss upon heating. Parameter *ab* decreases on heating for up to 5 h and then increases following further heating. In contrast, Fig. 5 shows that the time required to reach maximum adsorption rate during the adsorption experiments, ln[*t*], decreased after a peak at 3 h. These two parameters appear to contribute to weight loss in opposite ways. The relationship between them is shown in Fig. 6, which shows how heating time affects the adsorption process. The maximum adsorption rate, *ab*, decreased markedly prior to 3–5 h, but the corresponding parameter ln[*t*] showed little change. Over longer heating times, the *ab* decreased linearly with ln[*t*].

Considering changes in adsorption behavior with heat treatment reported previously,[6] the results shown in Figs. 5 and 6 indicate qualitatively that changes in both the chemical composition and the ultrastructure of bamboo can affect

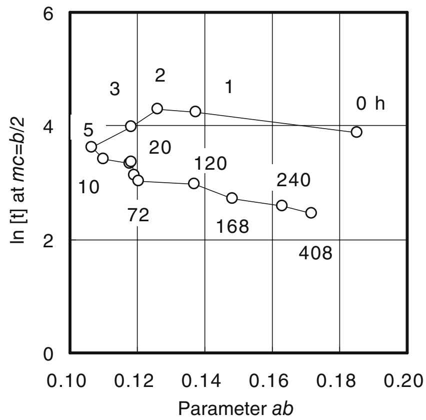

Fig. 6. Relationship between *ab* and the time to achieve the maximum adsorption rate, ln[*t*]

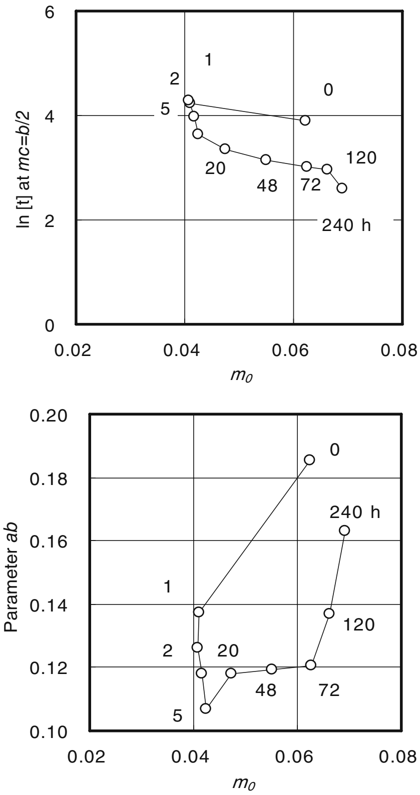

Fig. 7. Relationships between *ab* and m_0 derived from the Dubinin and Radushkevich theory (*bottom*) and between ln[*t*] at $mc = b/2$ and m_0 derived from the Dubinin and Radushkevich theory (*top*). m_0 describes the limiting volume of the adsorption space; that is, the saturated moisture content of the capillaries

adsorption behavior. The two factors responsible can be summarized as a decrease in hydroxyl groups that provide adsorption sites and the formation of capillaries due to gasification of the bamboo. The results shown in Fig. 6 suggest that the former factor plays the main role in samples heated for less than 5 h, with the latter affecting samples heated for over 5 h.

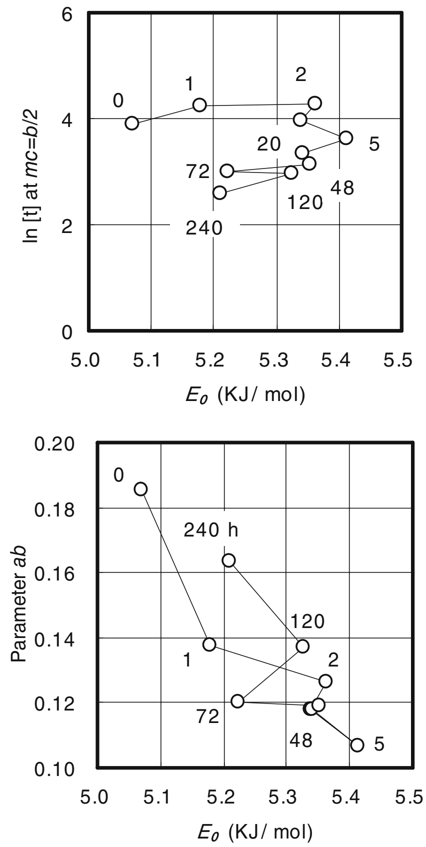

Fig. 8. Relationships between *ab* and E_0 derived from Dubinin and Radushkevich theory (*bottom*) and between ln[*t*] at $mc = b/2$ and E_0 derived from Dubinin and Radushkevich theory (*top*). E_0 is related to the characteristic adsorption energy

Logistic equation parameters compared with those derived from Dubinin and Radushkevich theory

In our previous study,[6] the isotherms resulting from bamboo heated to 200°C in air were analyzed using the Hailwood and Horrobin theory and Dubinin and Radushkevich theory,[7–9] and the parameters describing the adsorption characteristics were evaluated. The parameters derived in the present study show an inflection point at a heating time of about 5 h and hence are correlated with those reported previously. Therefore, they may be compared. The Dubinin and Radushkevich parameter m_0 is related to the amount of saturated adsorption (the micropore volume), and E_0 is a characteristic of the interaction energy.

Figure 7 shows plots of *ab* and ln[*t*] against m_0. Parameter *ab* increases and ln[*t*] decreases with m_0 for sample heated for more than 5 h. Hence, as may be expected, an adsorbate with large micropore volume, and hence large saturated adsorption capacity, will have a high rate of adsorption. Both parameters show different trends at 5 h, which can be attributed to a change in the properties of heat-treated moso bamboo after 5 h, as discussed previously. A plot of *b* against m_0 shows a similar trend as parameter *ab* with an inflection at 5 h. At this point, the number of hydroxyl groups, and hence potential adsorption sites, is decreased while gasification of the bamboo begins to increase with formation of micropores.[10] These changes in bamboo as an adsorbent due to heating time divide the plot into two parts. ln[*t*] also corresponds to the heating time of maximum rate of adsorption.

Plots of *ab* and ln[*t*] against parameter E_0 derived from Dubinin and Radushkevich theory are shown in Fig. 8, and indicate that *ab* decreases with increasing E_0 with the trend of the plot also changing at 5 h. The plots of ln[*t*] vs E_0 and m_0 show opposite trends but both show inflection at 5 h. In our previous report, we noted that E_0 decreases and m_0 increases upon further heating. Presumably, the adsorption rate increases with further changes in ultrastructure under more severe conditions.

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