Water adsorption process of bamboo heated at low temperature

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Abstract

The water adsorption capacities of moso bamboo samples heated at 200°C for various times were evaluated following their conditioning in a closed container at 97% relative humidity (RH) 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 hr heating. Before 5 hr heating, hydroxyl groups provided the main adsorption sites but their numbers decreased on heating. After 5 hr,-gasification of the bamboo increased and capillaries formed.

Keywords: **Water, Adsorption, Adsorption process, Heating, Bamboo, Logistic Regression Analysis, Dubinin - Rudshkevich Theory**

1. 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 mild heating only. 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.

2. Experimental

The same samples of 6-year-old moso bamboo (*Phyllostachys pubescens*; harvested in October 2004 in Shimane Prefecture in Japan) as used in our earlier study 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 hr prior to heat treatment and then heated at 200°C for 0 (untreated sample used as a control), 1 (ln1=0), 2 (ln2=0.69), 3 (ln3=1.10), 5 (ln5=1.61), 20 (ln20=3.00), 48 (ln48 =3.88), 72 (ln72=4.28), 120 (ln120=4.79), 240 (ln240=5.48), or 360 hr (ln360=5.89). Heating times were determined to allow the 11 data points to be plotted at nearly 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 100°C.

Samples were placed in a desiccator with a saturated solution of K_2SO_4 to provide 97% RH and their weight 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.

3. Results and Discussion

3.1. Regression Curves of Adsorption Process

The results of adsorption by the heat-treated bamboo are shown in Figure 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 almost agreed with experimental data for each heat-treated sample, stabilized sample obtained under the same isothermal experimental conditions.

The logistic equation used is the solution of the nonlinear differential equation was 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:

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

The maximum value of adsorption rate *dy/dx* was then given by ab/4 and the solution of equation (1) was:

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

As equation (3) can be transformed into 1/*y*=(1/*b*)+(*c*/*b*)exp[-*ax*], parameters *a*, *b*, and *c* may be determined easily. These parameters characterize the curves in the absorption process described by equation (3).For an equilibrium moisture content, *b* denotes the value when the curve is stabilized, i.e., the 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 *b* 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. As 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 Figure 2. The differential curves are normalized to make the maximum rate of adsorption equal to unity. The logistic curves shown in Figure 2 suggest that they may be placed into two groups: those heated for less than 3-5 hr and for more than this time. 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 hr.

3.2. 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 hr. This point corresponds with that found from analysis of isotherms, as reported in our previous paper[6].

The behavior of the equilibrium moisture content, denoted here by *b*, was reported elsewhere[6]. In this previous study, we showed that the equilibrium moisture content against heating time causes the minimum peak after heating for 2-5 hr 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 hr and then increases following further heating. In contrast, Figure 5 shows that the time required to reach maximum adsorption rate during the adsorption experiments, ln[*t*], decreased after a peak at 3 hr. These two parameters appear to contribute to weight loss in opposite ways. The relationship between them is shown in Figure 6, which shows how heating time affects the adsorption process. The maximum adsorption rate parameter, *ab*, decreased markedly prior to 3-5 hr, but the corresponding parameter ln[*t*] showed little change. Over longer heating times, the parameter *ab* decreased linearly with ln[*t*].

Considering changes in adsorption behavior with heat treatment reported previously[6], the results shown in Figures 5 and 6 indicate qualitatively that changes in both the chemical composition and ultrastructure of bamboo can affect adsorption behavior. The two factors responsible can be summarized as a decrease in the hydroxyl groups that provide adsorption sites and the formation of capillaries due to gasification of the bamboo. The results shown in Figure 6 suggest that the former plays the main role in samples heated for less than 5 hr, with the latter affecting samples heated for over 5 hr.

3.3. Logistic equation parameters compared with those derived from the 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 hr 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, i.e., the micropore volume, and E_0 is a characteristic of the interaction energy.

Figure 7 shows a plot of *ab* and ln[*t*] against m_0. This figure shows that parameter *ab* increases and parameter ln[*t*] decreases with m_0 for sample heated for more than 5 hr. Hence, as may be expected, an adsorbate with large micropore volume, and hence large saturated adsorption capacity, will have a large rate of adsorption. Both parameters show different trends at 5 hr, which can be attributed to a change in the properties of heat-treated moso bamboo after 5 hr, as discussed previously. At this point, the numbers of hydroxyl groups, and hence potential adsorption sites, will have decreased while gasification of the bamboo began 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 Figure 8, and indicate that *ab* decreases with increasing E_0 with the trend of the plot changing again at 5 hr. The plots of ln[*t*] vs. E_0 and m_0 show opposite trends but both show inflection at 5 hr.

Comparison between the parameters of the logistic equation and those of Dubinin and Radushkevich theory showed that the rate of water adsorption is strongly dependent on the parameters E_0 and m_0. 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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Captions

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

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

Fig. 3. Weight loss dependence of the parameters *a*, *b*, and *c* of regression curves derived from the logistic function $f(x)=b/(c+\exp[-ax])$: $f(x)=mc$ and $x=\ln[t]$.

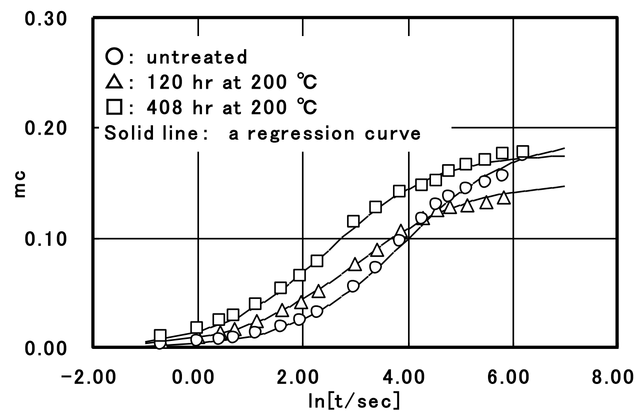
Fig. 4. Relationship between the parameter *ab* describing the maximum adsorption rate and weight loss.

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

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

Fig. 7 Relationship between the parameters *ab* and ln[*t*] at *mc*=*b*/2 and the parameter m_0 derived from the Dubinin and Radushkevich theory. m_0 describes the limiting volume of the adsorption space i.e., the saturated moisture content of the capillaries.

Fig. 8. Relationship between parameters *ab* and ln[*t*] at mc=b/2 and the parameter E_0 derived from Dubinin and Radushkevich theory. E_0 is related to the characteristic adsorption energy.



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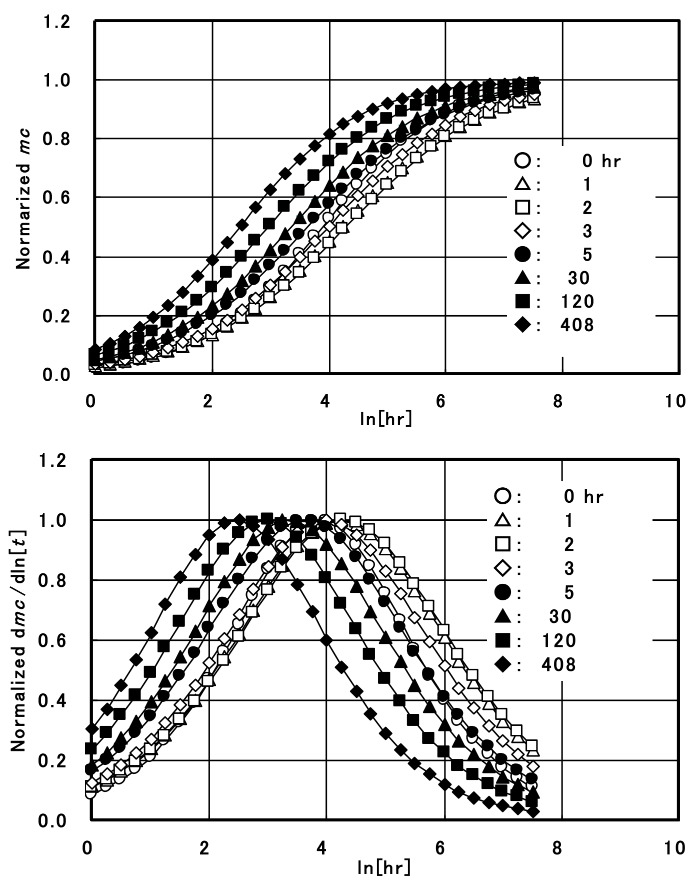

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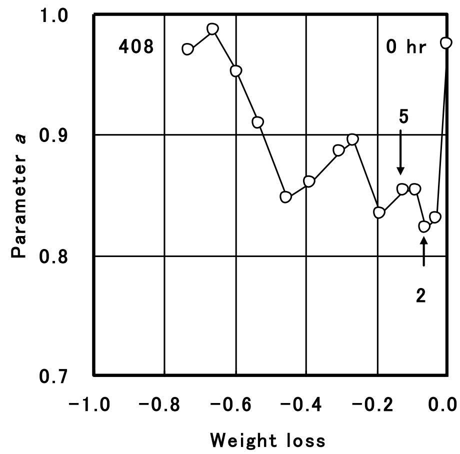

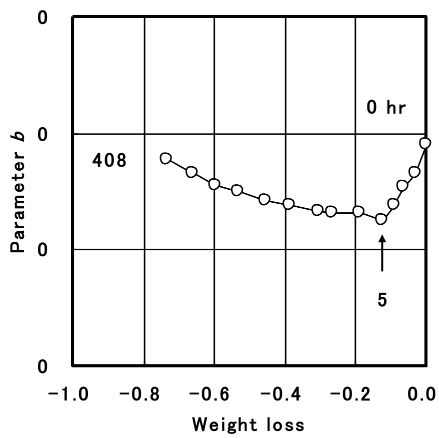

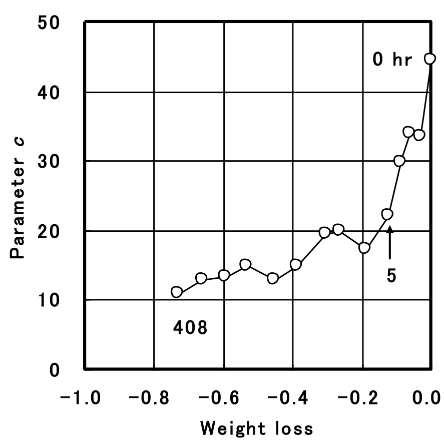

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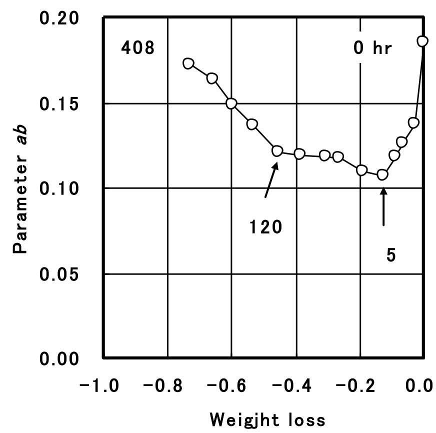


Fig. 4. Relationship between the parameter *ab* describing the maximum adsorption rate and weight loss.

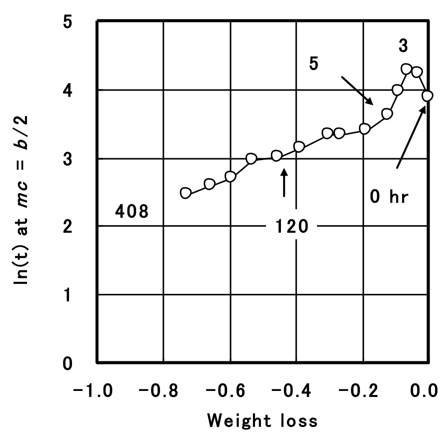


Fig. 5. Relationship between the time to achieve maximum adsorption rate, ln[*t*], and weight loss.

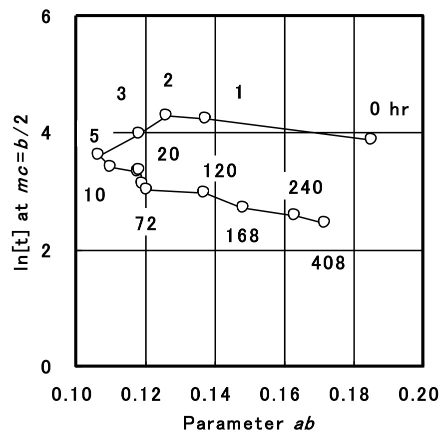
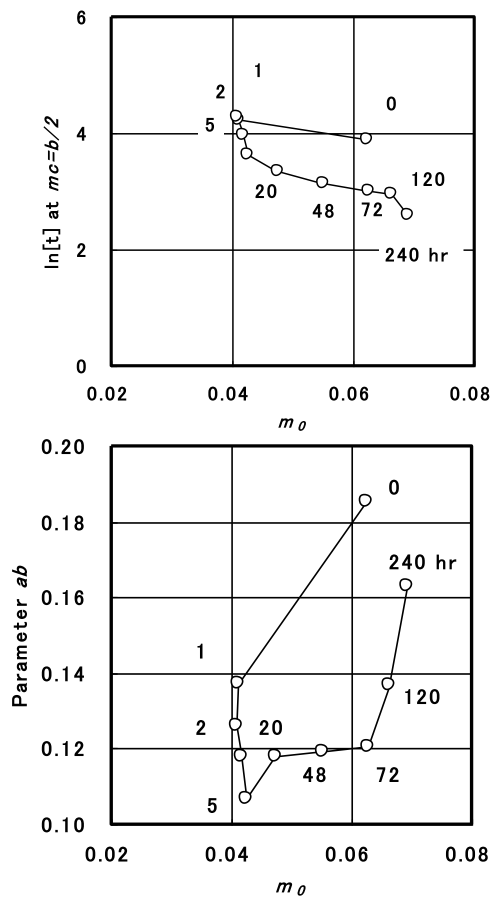


Fig. 6. Relationship between the parameter *ab* describing the maximum adsorption rate and the time to achieve the maximum adsorption rate ln[*t*].



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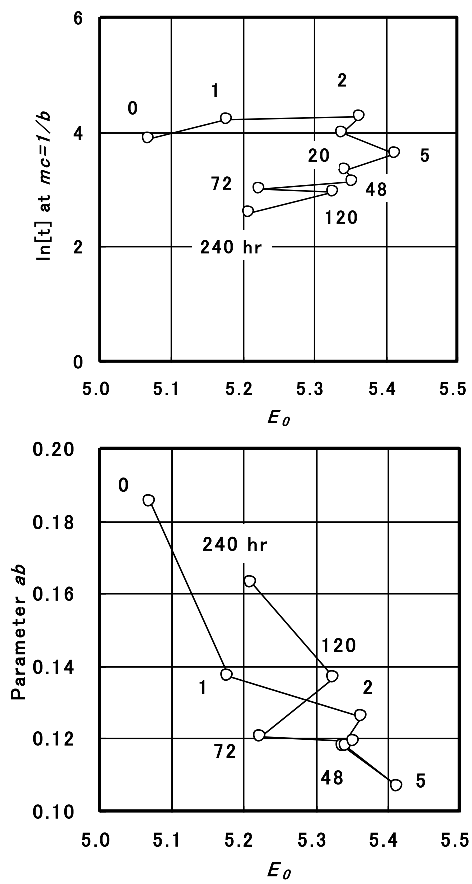

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