Relationship between Surface Polarity and Moisture Control onto Carbonaceous Materials Produced from Bean Curd Lees

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Abstract: In order to promote the shift to zero emissions of organic wastes, it is necessary to create carbon cycling processes. On the other hand, one of the distinguishing features of the Japanese climate is its high humidity, and an adsorbent which is high ability of moisture control are needed to prevent putrefaction of wood and keep indoor spaces at a comfortable humidity. This research focused on producing a carbonaceous material produced from bean curd lees, which is a form of food waste, and studied the relationship between the surface polarity or specific surface area of carbonaceous material, and the ability of moisture control. The specific surface area of the carbonaceous material was measured, and the highest value was exhibited in carbonaceous material produced at a temperature of 1173K. From this result, it appears that a microstructure develops as the carbonization temperature increases, but when the carbonization temperature is increased further, the specific surface area decreases due to merging of pores. Also, the ability of moisture control of charcoal is 22, and the ability of moisture control of the carbonaceous material produced from bean curd lees is a maximum of 198. This suggests that the material can be used in applications as a moisture control material. This work clarified that the ability of moisture control of the carbonaceous material increases to the degree that there are fewer phenolic hydroxyl groups and carboxyl groups in the carbonaceous material surface.

Key words: moisture control, bean curd lees, carbonaceous material, polarity group

1 Introduction

In recent years, increasing priority has been placed on the concept of “zero emissions”, where wastes are recycled and effectively used. However, in order to further promote zero emissions, it is necessary to create carbon cycling processes (1-3). If waste is converted to carbonaceous material, it is possible to reduce atmospheric emissions of carbon dioxide equivalent to the carbon content in the carbonaceous material. It is desirable for a carbonaceous material made from organic waste to have greater functionality -- i.e. the ability of

moisture control superior to previous materials. Also, carbonaceous material which is produced at a lower carbonization temperature will be a less expensive carbon material. The recycling of coffee grounds by carbonization was reported (4-8). We reported the adsorption characterization of water onto carbonaceous materials produced from coffee grounds and oolong tea leaves as vegetable biomass (9).

Activated carbon has been used as an adsorbent in various industrial fields, including solvent recovery, gas separation, catalysts, deodorization, and moisture control (10, 11). Moisture control adsorbents are common-

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ly used in Japan due to the high humidity, and charcoal has previously been used for this purpose. Excessive humidity causes condensation, mildew and outbreaks of mites. Rotting of the wood parts of foundations also causes deterioration of homes. Therefore, in Japan it is crucial to develop the adsorbents, which is high ability of moisture humidity, to remove excess moisture and maintain comfortable humidity. By maintaining a comfortable humidity, it is possible to control outbreaks of mildew and mites, and thus prevent allergies and save air-conditioning costs by making the summer cooler and the winter warmer, thereby contributing to energy conservation. Furthermore, comfortable humidity levels have recognized effects in promoting the health of people, i.e. by promoting metabolism and sound sleep, making the body feel lighter, and facilitating quick recovery from fatigue.

In this study, bean curd lees (a food waste) was carbonized at different temperatures, and the relationship between its surface polarity or specific surface area, and the ability of moisture control, was evaluated and studied.

2 Experimental and Method

2.1 Materials

The bean curd lees used is dried at 383K for 15 h and the composition is For the carbonization, 10 g of dried commercial bean curd lees was placed in a porcelain crucible, and kept at 773-1373K for 2 h in a muffle furnace, which was heated at a speed of 5 K/min. Charcoal was gone into commercial production and was produced from *Quercus phillyraeoides*. The specific surface area of the carbonaceous materials was found using BELSORP 40A (BEL JAPAN, INC., Osaka, Japan), that is, the specific surface area of the carbonaceous materials was calculated according to the nitrogen adsorption onto the carbonaceous materials was fitted to BET equation. Measurement of the surface pH of the carbonaceous materials was done using the method of Urano *et al.*(12) Carbonaceous material (0.5 g) was placed in an Erlenmeyer flask, and 100 mL of purified water was added. After boiling for 5 minutes, the fluid was cooled to room temperature, and the pH of the filtrate was measured using a HORIBA F-11 glass electrode type hydrogen ion concentration meter (HORIBA, Ltd., Kyoto, Japan)

2.2 Amount of Water Adsorbed/Desorbed onto Carbonaceous Materials

Carbonaceous materials (0.3 g) were measured in a weighing bottle, and left for 24 h in a desiccator kept at 293K with fixed humidity in **Table 1**. We confirmed that the water sorption onto the carbonaceous materials reached to equilibrium for 15 h. Then the weight of carbonaceous materials before and after adsorption was measured, and the amount of water adsorbed was calculated from the difference.

The saturated amount of adsorbed was calculated in a similar way, by leaving for 24 h in a desiccator kept at 293K and a relative humidity of 100%. To determine the amount of water desorbed, carbonaceous materials was placed in the saturation adsorption state at 293K and relative humidity of 100%, and the weight was measured, and then was kept in a desiccator, which the relative humidity was lowered to 95%, 84%, 78%, 66%, 52%, 42%, 32%, 20% and 15%. The desorption isotherm was calculated from the weight before and after desorption. For comparison, measurements were also done under the same conditions using charcoal produced from *Quercus phillyraeoides*. The difference between the amount of water adsorbed at a relative humidity of 100% and the amount of water adsorbed at a relative humidity of 52% was taken to be the ability of moisture control.

2.3 Base Consumption of Carbonaceous Materials

Base consumption of carbonaceous materials was measured using the methods of Boehm and Voll (13, 14). That is, the base consumption was found by adding approximately 0.1 g of carbonaceous materials to 50 ml

Table 1 Moisture Control by Materials.

Materials	Relative humidity (%)
LiCl·H ₂ O	15
CH ₃ COOK	20
CaCl ₂ ·6H ₂ O	32
Zn(NO ₃) ₂ ·6H ₂ O	42
NaHSO ₄ ·H ₂ O	52
NaNO ₂	66
Na ₂ S ₂ O ₃ ·5H ₂ O	78
KBr	84
Na ₂ HPO ₄ ·12H ₂ O	95

of 0.1 mol/L sodium hydroxide aqueous solution (Wako Pure Chemical Co., Ltd., Osaka, Japan), shaking for 48 h at 298K, filtering and then titrating the filtrate with 0.1 mol/L sodium hydroxide aqueous solution (Wako Pure Chemical Co., Ltd., Osaka, Japan). Methyl red was used as the indicator.

3 Results

3.1 Physical Properties of Carbonaceous Materials

Table 2 shows the specific surface area, the pore volume, surface pH and the base consumption for carbonaceous materials. The results indicate that the specific surface area of carbonaceous material produced at 973K or less was extremely low, but even though there was an increase in specific surface area of carbonaceous material produced at 1173K or higher, there was a decrease in the specific surface area of carbonaceous material produced at 1273K or higher. The pore volume of the carbonaceous material is correlated to the specific surface area of them. The surface pH value was in the range 9.1 to 10.1, and the pH value rose to the degree that the carbonaceous material was produced at a higher temperature. Base consumption is measured the number of functional groups on the carbonaceous material surface, and corresponds in particular to phenolic hydroxyl and carboxyl groups (13, 14). In terms of base consumption, a declining trend was evident in carbonaceous materials made at higher temperatures, and for carbonaceous material produced at a temperature of 1173K or higher, the value became negative. Therefore, it is thought that the surface polarity of carbonaceous material decreases when the material is produced at

higher carbonization temperature. Base consumption of some carbonaceous materials was negative value because bean curd lees contain much protein, many kinds of basic amino acids.

3.2 Adsorption/Desorption Isotherms of Water onto Carbonaceous Material

Figure 1 shows the adsorption/desorption isotherms of water onto carbonaceous materials. In the results, a sudden increase in the amount of water adsorbed to charcoal was evident for relative humidities of 0-50%, but no increase in the amount of water adsorbed was seen for relative humidities of 50-100%. On the other hand, the amount of water desorbed onto charcoal was almost the same as the amount of water adsorbed for relative humidities of 60-100%, and hysteresis was evi-

Fig. 1 Adsorption/Desorption Isotherms of Water onto Charcoal.

▼: Adsorption, ●: Desorption

Table 2 Physical and Chemical Properties of Carbonaceous Materials.

Samples	Specific surface area (m ² /g)	Pore volume (mL/g)	Surface pH	Base consumption (mmol/g)
773 K	1.9	0.006	9.1	0.012
873 K	1.9	0.006	9.7	0.012
973 K	3.3	0.008	9.7	0.009
1073 K	44.7	0.022	9.8	0.003
1173 K	67.0	0.032	10.1	−0.016
1273 K	11.0	0.015	9.6	−0.035
1373 K	7.8	0.011	10.1	−0.023
Char	35.0	0.116	6.8	0.016

dent in the range 0-60%.

Figure 2 shows the adsorption/desorption isotherms of water onto carbonaceous material, which is produced from bean curd lees at 773K. In the results, the adsorption isotherm has an “S” shape, and the amount of water adsorbed exhibited a lower value than the amount of water desorbed over the entire humidity range. Also, the amount of water adsorbed/desorbed onto the carbonaceous materials, which were produced from bean curd lees, exhibited a higher value than that of water onto charcoal. On the other hand, hysteresis was evi-

dent over the entire relative humidity range, and it was found that desorption by the carbonaceous materials, which were produced from bean curd lees, was more difficult after water adsorption.

Figures 3-5 show the adsorption/desorption isotherms of water onto the carbonaceous materials, which are produced from bean curd lees at 873 to 1073K. In the results, the amount adsorbed gradually increases just as with carbonaceous material, which is produced at 773K in the low relative humidity range. Also, the amount of water adsorbed onto the carbona-

Fig. 2 Adsorption/Desorption Isotherms of Water onto Carbonaceous Material, which was Produced from Bean Curd Lees at 773K.
▼: Adsorption, ●: Desorption

Fig. 4 Adsorption/Desorption Isotherms of Water onto Carbonaceous Material, which was Produced from Bean Curd Lees at 973K.
▼: Adsorption, ●: Desorption

Fig. 3 Adsorption/Desorption Isotherms of Water onto Carbonaceous Material, which was Produced from Bean Curd Lees at 873K.
▼: Adsorption, ●: Desorption

Fig. 5 Adsorption/Desorption Isotherms of Water onto Carbonaceous Material, which was Produced from Bean Curd Lees at 1073K.
▼: Adsorption, ●: Desorption

ceous material, which is produced from bean curd lees at 873K and 973K, increases and the amount of water desorbed decreases, compared to carbonaceous material, which was produced at 773K with relative humidity of 70% or more, and the hysteresis was larger than that of charcoal and carbonaceous material, which was produced at 773K.

Figures 6-8 show the adsorption/desorption isotherms of water onto the carbonaceous material, which is produced from bean curd lees at 1173 to 1373K. In the results, the adsorption isotherm of water

Fig. 6 Adsorption/Desorption Isotherms of Water onto Carbonaceous Material, which was Produced from Bean Curd Lees at 1173K.
▼: Adsorption, ●: Desorption

Fig. 7 Adsorption/Desorption Isotherms of Water onto Carbonaceous Material, which was Produced from Bean Curd Lees at 1273K.
▼: Adsorption, ●: Desorption

has an “S” shape, and, more specifically, there is a sudden increase in the amount of water adsorbed near the saturated relative humidity. On the other hand, hysteresis is evident in the entire relative humidity range.

3.3 Ability of Moisture Control of Carbonaceous Material Produced from Bean Curd Lees

Table 3 shows the ability of moisture control of charcoal and carbonaceous material, which is produced from bean curd lees. The results show that the ability of moisture control of carbonaceous material, which was produced from bean curd lees, was higher than that of charcoal.

Figure 9 shows the relationship between base consumption and the ability of moisture control by carbonaceous materials which were produced from bean curd lees. In the results, a negative correlation with a correlation coefficient of 0.966 [(base consumption) = -0.000408 (ability of control humidity) + 0.05172] was evident between base consumption and the ability of moisture control.

4 Discussion

The specific surface area of the carbonaceous material was measured, and the highest value was exhibited in carbonaceous material, which was produced at a temperature of 1173K. From this result, it appears that a microstructure develops as the carbonization tempera-

Fig. 8 Adsorption/Desorption Isotherms of Water onto Carbonaceous Material, which was Produced from Bean Curd Lees at 1373K.
▼: Adsorption, ●: Desorption

Table 3 Ability of Moisture Control of Carbonaceous Materials.

Samples	Amount of water adsorbed (mg/g)		
	at relative humidity 100%	at relative humidity 52%	Moisture control (%) ^{a)}
773 K	191	93	98
873 K	211	97	114
973 K	203	99	104
1073 K	204	101	103
1173 K	291	120	171
1273 K	312	114	198
1373 K	296	103	193
Char	136	113	22

^{a)} (Amount of water adsorbed at relative humidity 100%) – (Amount of water adsorbed at relative humidity 52%)

Fig. 9 Relationship between Base Consumption and Ability of Moisture Control Humidity.

ture increases, but when the carbonization temperature is increased further, the specific surface area decreases due to merging of pores. From the results on the adsorption isotherms of water onto carbonaceous materials, which were produced in the range 773 to 1373K, it was found that adsorption behavior is almost the same, but the saturated amount of water adsorbed increases together with the carbonization temperature. On the other hand, it became clear that the hysteresis onto carbonaceous materials, which are produced at a higher carbonization temperature, is large, and thus it is difficult to desorb water molecules which have been adsorbed.

The ability of moisture control of carbonaceous material, which was produced from bean curd lees, was higher than that of charcoal. No relationship was evident between the specific surface area and the ability of moisture control of the carbonaceous material. The

ability of moisture control of the carbonaceous materials, which were produced from bean curd lees, was 4.5–9.0 times that of charcoal. More specifically, the ability of moisture control was greater for materials with smaller base consumption, and carbonaceous material, which was produced at 773K, exhibited the ability of moisture control approximately 4.5 times that of charcoal.

The relationship between base consumption and the ability of moisture control was a negative correlation (a correlation coefficient is 0.966). This suggests that reduction of phenolic hydroxyl groups and carboxyl groups in the surface increases the ability of moisture control. It has been reported that phenolic hydroxyl groups and carboxyl groups form hydrogen bonds with water molecules, and that the bonding strength is 5–10 times that of the Van der Waals strength (15). This result is thought to be because it is difficult to desorb water molecules which have been adsorbed if there are polar groups present in the carbonaceous material surface.

5 Conclusions

This paper studied the relationship between surface polarity and moisture control performance of the carbonaceous materials, which were produced from bean curd lees at different carbonization temperatures. The research clarified that the bond strength between water molecules and polar groups in the carbonaceous material surface increases and the ability of moisture control decreases as the number of phenolic hydroxyl and carboxyl groups in the surface increases. Also, it is possible to make carbonaceous materials with high ability of

moisture control by carbonization of bean curd lees, which is an organic waste.

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