

## ORIGINAL ARTICLE

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## Pore structure and adsorption properties of carbonized material prepared from waste paper

Received: June 23, 2000 / Accepted: January 17, 2001

### Abstract

We have already reported the adsorptivity and pore structure of activated carbon made from waste newspaper in order to use the waste paper for purposes other than paper-making stock. However, manufacturing the activated carbon may not necessarily be an advantageous method based on environmental concerns and the effective use of the resource because the reaction during the activating process is endothermic and the amount of carbon consumed is significant. Here, we examine the pore structure and adsorption properties of waste newspaper used as an adsorbent in the form of a carbonized material. Waste newspaper was carbonized for 2 h in the temperature range 400°–1000°C. The specific surface area of the carbonized material obtained, 418 m<sup>2</sup>/g, was highest for the sample carbonized at 800°C, which was equal to or greater than that of commercially available charcoal. Moreover, the iodine adsorption number of 581 mg/g was the highest and the rate of adsorption was the fastest for the sample carbonized at 800°C. However, the humidity control capability was highest for the material carbonized at 600°–700°C. It has been determined that it is advantageous to carbonize waste paper at 800°C in order to use the carbonized material as an adsorbent, while carbonization at 600°–700°C is more advantageous for use as a humidity control material.

**Key words** Waste paper · Carbonized material · Adsorption · Porous structure

### Introduction

Recently, activated carbon has been used in many areas, including the control of air pollution, water pollution, noxious odors, environmental protection, and advanced wastewater treatment. Therefore, research into obtaining activated carbon from raw materials such as waste wood,<sup>1</sup> organic waste sludge,<sup>2</sup> bean-curd refuse,<sup>3</sup> bagasse,<sup>4</sup> walnut shells,<sup>5</sup> waste phenol resin<sup>6</sup> has been carried out as part of the recycling of organic-type wastes. We have also made activated carbon using waste newspaper as the raw material. This was one of several recycling methods being tested, but the papermaking stock of the waste paper was not included. We reported that this product had almost the same adsorptivity as commercially available activated carbon.<sup>7</sup> Activated carbon is made from a carbonaceous material such as coal or charcoal that is decomposed by an activating treatment performed with steam and carbon dioxide at temperatures higher than 850°C, during which the pores, which are an important factor for the adsorptivity of the surface of the carbon, develop. However, manufacturing activated carbon may not necessarily be an advantageous method from the aspect of environmental concerns and an effective use of the resource, since the reaction for the activating treatment is endothermic,<sup>8</sup> which means significant energy consumption, and the amount of carbon consumed is very high.

On the other hand, although charcoal has long been used as a fuel, a new use which utilizes the adsorptivity of charcoal has recently been developed, and its water purification properties,<sup>9</sup> pore structure, and adsorptive properties<sup>10,11</sup> are currently under review. Furthermore, carbonized material with waste wood as the raw material has been used as a humidity control material under the floors of homes.<sup>12</sup> As the pyrolysis of wood and cellulose in an inert gas is an exothermic reaction,<sup>13</sup> utilizing carbonized material from waste wood and waste paper as the raw material is thought to be advantageous from the aspect of energy consumption.

Therefore, it is very desirable to utilize waste paper as the raw material for carbonized adsorbents, except for

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papermaking. The pore structure and adsorptivity of charcoal varies according to the carbonizing temperature.<sup>11</sup> Therefore, it is possible to make a charcoal which is suitable as an adsorbent by controlling the carbonizing temperature. With carbonized material made from waste paper, although it is considered possible to adjust the adsorptivity by controlling the carbonizing temperature, as with charcoal, the relations between the carbonizing temperature for waste paper, the pore structure, and the adsorptivity of the carbonized material have not been rigorously examined. Accordingly, the purpose of this study was to obtain some basic data in order to utilize carbonized waste paper as an adsorbent. Phenol resin was added to crushed waste newspaper, and the mixture was hot-pressed into a board. The material was then prepared by heating the board at 400°–1000°C in a nitrogen gas stream. The relationships between the carbonizing temperature and the chemical composition, pore structure, and adsorption properties of the carbonized material were examined for carbonized materials prepared at various temperatures.

## Experimental

### Trial manufacturing of carbonized material

Recyclable waste newspaper was cut into small pieces of about 10mm using a crosscut shredder and phenol resin was added at 8%. The mixture was poured into a mold, hot-pressed for 10min at 2Mp and 150°C, and then molded into a board 6mm thick. The density of the board was adjusted to 0.7 g/cm<sup>3</sup> by adjusting the amount of raw material poured in. This waste paper board was cut into 25mm × 25mm pieces and used as the sample for carbonization.

The sample was placed in the carbonizing furnace, which is a 90-mm-diameter stainless steel tube in a tubular furnace, and to eliminate the oxygen in the carbonizing furnace, evacuation and nitrogen substitution was repeated three times. The carbonization conditions included the temperature of the carbonizing furnace, which was increased at a rate of 10°C/min in the nitrogen gas stream, kept at a predetermined temperature within the range 400°–1000°C for 2h, and then quickly cooled.

### Chemical composition of carbonated material

#### *Elementary analysis*

The amounts of carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) were measured using an elementary analysis apparatus (CHN Corder model MT-5, made by Yanaco Analytical Instruments, Tokyo, Japan). The amount of oxygen was calculated from the difference between the mass of the organic part except for the ash content and the total mass of C, H, and N.

#### *Ash content measurement*

The measurement method conformed to the ignition residue measurement method of JIS-K-1474 (method of testing activated carbon). About 1–2g of the sample was weighed in a crucible, the temperature was gradually increased in the electric furnace, and the sample was incinerated at 900°C for 1h. Afterwards, it was quickly cooled, and the ash content was calculated from the residual mass.

#### *Elementary analysis of ash content*

The residue from the ash content measurement was used as the sample. This was formed into a disk by pressing, and a semiquantitative analysis (using the fundamental parameter method for all elements having an atomic number greater than boron) was carried out using a fluorescent X-ray analyzer (Model RIX-3000, made by Rigaku, Tokyo, Japan).

#### *pH measurement*

The measurement conformed to the pH value measurement method of JIS-K-1474 (method of testing activated carbon). That is, a 1-g sample was charged in 100ml water, heated, and boiled gently for 5min. After it was cooled to room temperature, it was filled to a final volume of 100ml by adding water, and the pH value was measured using a pH meter (Model 691, made by Metrohm, Tokyo, Japan).

#### *Measurement of the amount of eluted organic carbon*

After 1g of the carbonized material was charged into 50ml distilled water and shaken at 23°C for 168h, the particles of carbonized material were removed by filtration. The amount of organic carbon eluted into the aqueous solution was measured by a total organic carbon analyzer (Model TOC-8L, made by Yanagimoto Manufacturing, Tokyo, Japan).

### Structure of carbonized material

#### *Pore structure*

Carbonized materials prepared at various temperatures were crushed to a particle diameter of less than 53μm and used as the samples. Palm-shell activated carbon used for refrigerator deodorants (made by Hakuden, Tokyo, Japan) and reagent-grade activated carbon (made by Kanto Chemical, Tokyo, Japan) were used as samples for comparison. The adsorption isotherm of nitrogen at liquid nitrogen temperature was obtained using a constant-volume adsorption apparatus (Belsorp18, made by Japan Bell, Osaka, Japan). Based on these data, the specific surface area was obtained by a BET plot within the relative pressure range 0.05–0.15,

**Table 1.** Yield and elemental analysis of waste-paper carbonized materials

Symbol for carbonized material	Carbonization temperature (°C)	Carbonized material yield (wt. %)	Composition (wt. %)				Empirical formula (ref. to C6)
			C	H	O	Ash	
Untreated	Untreated	–	43.1	5.4	47.7	3.8	C6 H9.0 O5.0
400	400	43.8	60.9	4.1	26.1	8.9	C6 H4.8 O1.9
500	500	34.9	67.9	3.1	17.9	11.1	C6 H3.3 O1.2
600	600	31.7	70.9	2.3	14.7	12.1	C6 H2.3 O0.9
700	700	29.2	70.9	1.7	14.6	12.8	C6 H1.7 O0.9
800	800	27.3	71.1	1.2	14.1	13.7	C6 H1.2 O0.9
900	900	26.9	72.2	0.9	12.9	14	C6 H0.9 O0.8
1000	1000	26.4	72.2	0.8	12.8	14.2	C6 H0.8 O0.8

and the pore distribution curve was obtained by the Dollimore–Heal method.<sup>14</sup> To measure the pore distribution and the pore volume of pores having a pore radius of 3 nm or more, the trial-manufactured carbonized material was cut to a suitable size and measured in a block-shaped sample using a mercury penetration-type pore distribution measurement apparatus (Pore sizer 9320, made by Micromeritics, Atlanta, GA, USA).

#### Adsorption properties of carbonized material

##### *Amount of adsorbed acid and alkali*

Based on the method of Abe and co-workers,<sup>10</sup> 1 g of the sample, which was crushed to less than 53  $\mu\text{m}$ , was added first to 100 ml of 0.1 N hydrochloric acid (HCl) and then to an aqueous solution of sodium hydroxide (NaOH). After shaking for 168 h at 23°C and allowing the mixture to adsorb, the particles of carbonized material were removed by filtration. The amount absorbed was obtained by reverse titration of the filtrate.

##### *Iodine adsorption number*

A suitable amount of the sample was charged in 50 ml of a 150-mmol/l potassium iodide aqueous solution so that the iodine concentration became 50 mmol/l based on JIS-K-1474 (method of testing activated carbon). The solution was shaken at 23°C for 24 h and then left for 168 h for adsorption. The amount adsorbed was evaluated by measuring the adsorption isotherm of iodine from the amount of iodine remaining in the potassium iodide solution. The rate of adsorption of iodine was obtained from the residual concentration of iodine, which was measured by charging 1 g of the sample in 50 ml of the potassium iodide solution and shaking at 23°C for 0.5, 1, 3, 6, 24, 72, and 168 h.

##### *Amount of water vapor adsorbed*

The evaluation was carried out in a desiccator<sup>15</sup> by the saturated salts method by obtaining the adsorption isotherm in relative humidities of 20%, 33%, 58%, 75%, and 97% at

20°C. The humidity control capability of the carbonized material was evaluated using the method of Abe et al.<sup>16</sup> That is, the sample was put into a weighing bottle, which was placed in a temperature and humidity chamber (Model PL2, made by Tabai Espec, Osaka, Japan) and then kept in the water vapor at a relative pressure of 0.55 (W1), 0.90 (W2), or 0.55 (W3) at 25°C. (W2) – (W3) was evaluated as the humidity control capability (HCC) by obtaining the amount of water adsorption for each relative humidity.

## Results and discussion

### Chemical composition of carbonized material

#### *Changes in yield and C, H, and O elemental compositions of carbonized material due to the carbonizing temperature*

For cellulose and wood, decomposition, measured by thermogravimetry, commenced from approximately 200°C in a nitrogen atmosphere. A remarkable decrease in mass occurred at approximately 350°C, and the decrease in mass with the rise in temperature was gradual at temperatures higher than 350°C.<sup>17</sup> Accordingly, the carbonizing temperature in this study was set within the range 400°–1000°C.

Table 1 shows the carbonizing temperatures, yields of carbonized material, ash contents, and C, H, and O elements in the carbonized materials, and the empirical formulas of organic substances. The yield of carbonized material decreased, and ash content in the carbonized material increased as the carbonizing temperature increased. However, the decrease in yield resulting from increasing the carbonizing temperature was small at 800°C or higher.

In the organic part, the ratio of C increased and the ratios of H and O decreased as the carbonizing temperature increased. In particular, an increase in C and a decrease in O caused by increasing the carbonizing temperature were obvious at 600°C or lower.

#### *pH and amount of organic carbon eluted from carbonized material*

Table 2 shows the pH and the amount of organic carbon eluted from carbonized material prepared at various car-

**Table 2.** pH and dissolved organic carbon of waste-paper carbonized materials

Carbonized material	pH	Dissolved organic carbon (mg/l)
400	8.9	183
500	10.2	109
600	10.4	77
700	10.6	–
800	10.6	46
900	10.6	–
1000	10.6	36

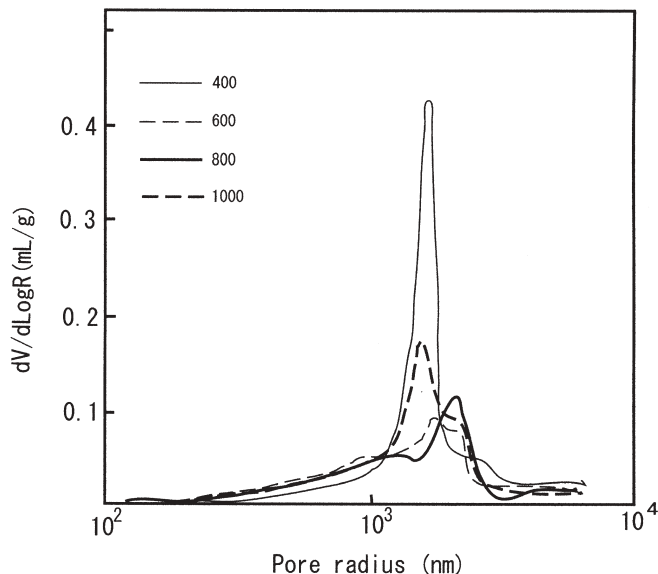
**Table 3.** Elemental analysis of waste-paper ash

Element	Content (wt. %)
C	5.8
O	40
Na	4
Mg	4.2
Al	12
Si	29
P	0.11
S	0.01
K	0.43
Ca	3.4
Ti	0.25
Cr	0.02
Mn	0.05
Fe	0.82
Cu	0.05

bonizing temperatures. The pH of the carbonized material indicated a weak alkaline condition with almost no change observed over 500°C. The amount of eluted organic carbon decreased as the carbonizing temperature increased. The reason for this phenomenon is that when the carbonizing temperature is low, the water-soluble uncarbonized material increases and is eluted. When the carbonizing temperature increases, it is thought that the amount of eluted organic carbon decreases owing to the decreasing amount of uncarbonized material.

#### Chemical composition of the ash content

A fluorescent X-ray analysis of the ash contents of the waste newspaper is shown in Table 3. To improve the printing property and brightness, and depending on its use, kaolin ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ), calcium carbonate ( $\text{CaCO}_3$ ), and white carbon ( $\text{SiO}_2$ ) are added to paper as inorganic fillers.<sup>18</sup> As paper is used for various applications, several kinds of paper suitable for each use are marketed, and they contain different kinds of fillers. In general, white carbon is added as an inorganic filler during the manufacture of newsprint. However, aluminum (Al), magnesium (Mg), and calcium (Ca) are included in the ash content of waste newspaper, and it is thought that these elements come from added kaolin, talc, calcium carbonate, and white carbon. Consequently, it can be postulated that various

**Fig. 1.** Pore distribution of waste-paper carbonized materials determined by mercury intrusion porosimetry**Table 4.** Pore volume, pore radius, and density obtained by mercury porosimetry

Carbonized material	Pore volume, $V_{\text{Hg}}$ (ml/g)	Pore radius, $R_{\text{Hg}}$ (nm)	Apparent density (g/ml)	True density (g/ml)
400	1.1	1580	0.521	1.395
500	1.17	1900	0.518	1.399
600	0.697	1240	0.652	1.437
700	0.487	1370	0.779	1.577
800	0.673	1270	0.697	1.625
900	–	–	–	–
1000	0.861	1470	0.588	1.688

types of paper other than newspaper are being recycled into newsprint.

#### Pore structure of carbonized material

##### Determination of pore structure by mercury intrusion porosimetry

Figure 1 shows the pore size distribution within the range 100–6500 nm measured by mercury intrusion porosimetry. The distribution curves for the various carbonizing temperatures are similar because they all peak around 2000 nm radius. Table 4 shows the apparent density, true density, total pore volume,  $V_{\text{Hg}}$ , obtained by mercury intrusion porosimetry, and pore radius,  $R_{\text{Hg}}$ , when the accumulated pore volume (starting from a large pore radius) becomes half of  $V_{\text{Hg}}$ .

$V_{\text{Hg}}$  decreased as the carbonizing temperature increased to 700°C, reached a minimum value of 0.49 ml/g at 700°C, and then increased as the temperature increased. The  $R_{\text{Hg}}$

value behaved similarly. When these results are compared with those from various charcoals,<sup>19</sup> the  $V_{Hg}$  was close to that of charcoal made from oak or Japanese oak. These results can be attributed to the fact that waste-paper board has a high  $R_{Hg}$  because it has relatively big pores compared with oak or Japanese oak, although the waste paper board which was used as the raw material had a density very close to that of oak or Japanese oak. Moreover, the apparent density increased as the carbonizing temperature increased, reached a maximum at 700°C, and decreased as the carbonizing temperature increased to 700°C or higher. However, the true density increased as the carbonizing temperature increased. The apparent density is a value affected by the pore volume in the carbonized material, and this coincides with the behavior of  $V_{Hg}$  caused by the carbonizing temperature. That is, it is thought that although the pore volume decreased and the apparent density increased because of shrinkage of the carbonized material as the carbonizing temperature increased to 700°C, the shrinkage was small for any temperature rise thereafter, and the pores increased because of the decreasing mass caused by the carbonization. Moreover, the reason for the increase in the true density with increasing carbonizing temperature is considered to be due to crystal growth<sup>20</sup> and the increasing carbon ratio due to the increase in temperature.

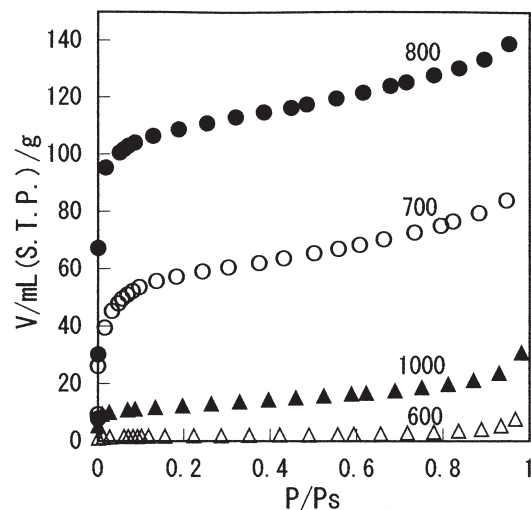
#### Determination of pore structure by the nitrogen-adsorption method

Figure 2 shows the adsorption isotherms with nitrogen at the temperature of liquid nitrogen for the waste paper carbonized material prepared at various carbonizing temperatures. In the carbonizing temperature range of 600°C or higher, the amount of adsorbed nitrogen increased as the carbonizing temperature increased, and reached a maximum at 800°C. For a carbonizing temperature of 800°C or higher, the amount of adsorbed nitrogen decreased. Moreover, the carbonized material prepared at 800°C showed a higher amount of adsorbed nitrogen at a very low relative pressure of nitrogen. Based on these results, it is thought that the carbonized material prepared at 800°C has the most developed pores.

Table 5 shows the total pore volumes  $V_N$  (ml/g) and average pore diameters  $D_N$  (nm) assessed by the nitrogen adsorption process, and the specific surface areas  $S_N$  (m<sup>2</sup>/g) of the waste-paper carbonized material and commercially available activated carbon. The shape of the pores was assumed to be cylindrical, and the average pore diameter  $D_N$  (nm) was obtained from the  $V_N$  and  $D_N$  values in the equation

$$D_N = 4000 V_N / S_N$$

The specific surface area and pore volume of the waste-paper carbonized material prepared at 400°–600°C were remarkably small. The specific surface area and pore volume significantly increased as the carbonizing temperature increased above 700°C, and the highest value was obtained at 800°C. In the range greater than 800°C, the spe-



**Fig. 2.** Adsorption isotherms of waste paper carbonized materials.  $V/ml$  is the volume of nitrogen at standard temperature (25°C) and pressure (101.2 kPa).  $P/P_s$  is the pressure relative to the saturation pressure of nitrogen

**Table 5.** Specific surface area and pore volume calculated from the adsorption isotherm of nitrogen

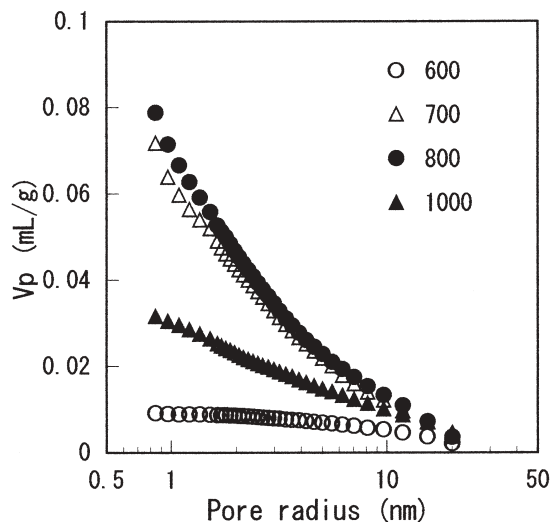
Carbonized material	Specific surface area, $S_N$ (m <sup>2</sup> /g)	Pore volume, $V_N$ (ml/g)	Mean pore diameter, $D_N$ (nm)
400	4.54	0.0115	10.1
500	5.91	0.0154	10.4
600	5.04	0.0108	8.57
700	207	0.132	2.55
800	418	0.216	2.07
900	94.2	0.0538	2.28
1000	43.4	0.0424	3.91
A	1040	0.473	1.82
B	1512	1.463	3.86

A, Palm-shell activated carbon; B, reagent-grade activated carbon

cific surface area and pore volume decreased as the carbonizing temperature increased. The specific surface area of the waste-paper carbonized material prepared at 800°C was greater than that of commercially available charcoal, which generally has a value of about 300–400 m<sup>2</sup>/g,<sup>11,21</sup> but it was approximately 30%–40% of commercially available activated carbon. The average pore diameter reached a minimum value at 800°C carbonizing temperature. This value was similar to that of commercially available activated carbon.

Figure 3 shows the pore volume distribution for pores with a radius of 1 nm or more. The pore volume of pores with a radius of 1 nm or more for the waste-paper carbonized material prepared at 600°C was very small. The pore volume of pores with a radius of 1–10 nm for the carbonized material prepared at 700° and 800°C was considerably larger than that of the carbonized material prepared at 600°C. As for the carbonized material prepared at 1000°C, the pore volume was greater than that of the carbonized





**Fig. 3.** Cumulative pore-volume distribution of waste-paper carbonized materials

**Table 6.** Adsorption of acid and bases onto waste-paper carbonized materials

Carbonized material	Amount adsorbed (mmol/g)	
	HCl	NaOH
400	0.305	–
500	0.621	0.308
600	0.81	0.268
700	1.19	0.233
800	1.327	0.198
900	0.994	0.223
1000	0.678	0.198

material prepared at 600°C although it was less than that of the carbonized material prepared at 700° and 800°C. In particular, for the carbonized material prepared at 700°–800°C, it is thought that the pore volume increases as the pore radius becomes smaller, and more pores with a radius of 1 nm or more developed compared with the carbonized materials prepared at other temperatures.

#### Adsorption behavior

##### *Adsorbed amount of acid and alkali*

The amounts of HCl and NaOH consumed, which indicates the chemical properties of the surface of the waste-paper carbonized material, are shown in Table 6. The amount of HCl consumption increased as the carbonizing temperature increased to 800°C. However, it decreased as the carbonizing temperature increased to over 800°C. The amount of NaOH consumed showed a tendency to decrease as the carbonizing temperature increased. This tendency was similar to that of charcoal.<sup>10,11</sup> For the waste-paper carbonized material prepared at 1000°C, a decrease was observed in the consumption of both HCl and NaOH. It is thought that the

**Table 7.** Adsorption rate of iodine by waste-paper carbonized materials

Carbonized material	24 h		168 h		
	$1/N_{24}$	$K_{24}$	$1/N_{168}$	$K_{168}$	$K_{24}/K_{168}$
400	0.645	132	0.349	303	0.574
500	0.673	75	0.328	282	0.381
600	0.97	28	0.408	148	0.321
700	0.15	349	0.0931	412	0.891
800	0.106	503	0.0885	536	0.954
900	0.628	69	0.382	115	0.744
1000	0.568	72	0.438	94	0.864

acid and base functional groups present on the surface of the waste-paper carbonized material were removed at this high temperature.

##### *Adsorbed amount and adsorption rate of iodine*

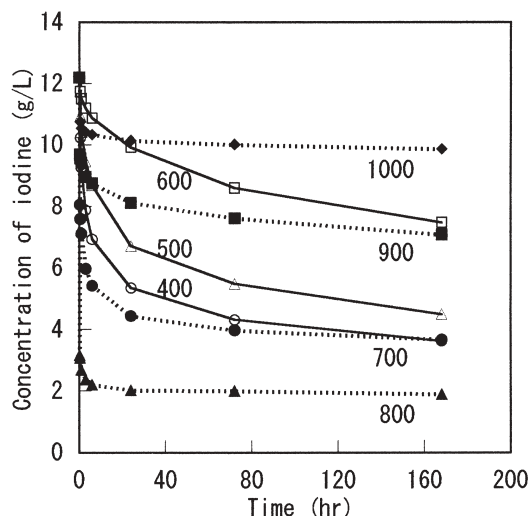
The adsorption isotherm of iodine from the potassium iodide aqueous solution was measured as an adsorption characteristic in the liquid phase. The adsorption times were 168 h, which was considered to be sufficient to reach equilibrium, and 24 h. The adsorption isotherms obtained were arranged using the Freundlich equation as follows:

$$\log X = \log K + (1/N)\log C$$

where  $C$  is the residual concentration (g/l) of iodine,  $X$  is the adsorbed amount for each unit mass (mg/g) of waste-paper carbonized material, and  $K$  and  $1/N$  are the adsorption constants.  $K$  is the amount of iodine adsorbed when the residual concentration of iodine is 1 g/l.  $1/N$  is the value which expresses the affinity between the adsorbent and adsorbate, the smaller its value, the higher the affinity.<sup>10</sup> The affinity depends on the molecular size of the adsorbate and the pore diameter, which both participate in the adsorption. The adsorbate has a higher affinity and smaller  $1/N$ , with the increase in the pore size being related to the diameter for the molecular size of the adsorbate. Table 7 shows the adsorption constants  $K$  and  $1/N$  of the waste-paper carbonized material obtained from the adsorption isotherm for 24-h and 168-h adsorption times. The  $K$  value decreased as the carbonizing temperature increased in the range 400–600°C. When the carbonizing temperature was 600°C or higher, the  $K$  value increased as the carbonizing temperature increased and became a maximum at 800°C, but it decreased at higher temperatures.

On the other hand,  $1/N$  decreased as the carbonizing temperature increased, became a minimum at 800°C, and then increased at higher temperatures. It is thought that many pores with diameters with a high affinity for iodine were formed at 700–800°C. However, at 900°C or higher, it is thought that the diameters of the pores became small, and the number of pores which were able to adsorb the iodine molecules decreased.

The ratio of  $K$  at 24 h and 168 h ( $K_{24}/K_{168}$ ) was also adopted as an index for the rate of adsorption. The ratio



**Fig. 4.** Relationship between iodine residual concentration in the iodine solution and iodine adsorption time for waste-paper carbonized materials

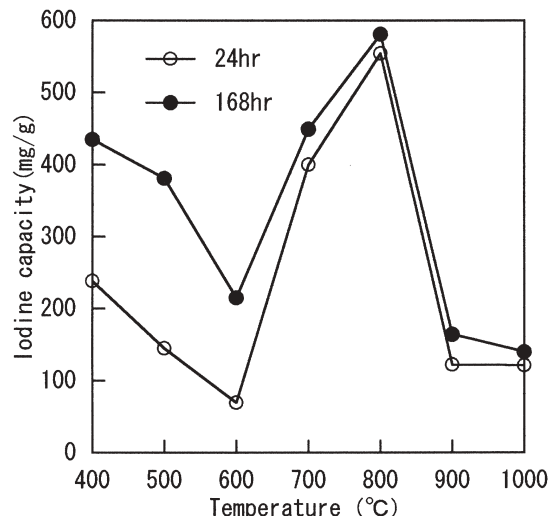
decreased as the carbonizing temperature increased within the range 400–600°C, increased as the temperature increased over 600°C, and became a maximum at 800°C. The ratio approached one at 700°C or higher, and the rate of adsorption increased.

To evaluate the effect of carbonizing temperature on the rate of adsorption in more detail, the relationship between the iodine adsorption time and the residual concentration of the iodine solution was examined (Fig. 4). In the waste-paper carbonized material prepared at a carbonizing temperature of 400°–600°C, the adsorption rate was low. On the other hand, adsorption approached an equilibrium within a short time for the carbonized material prepared at 700°C or higher. In particular, the adsorption almost reached equilibrium within 3 h for carbonized material prepared at 800°C.

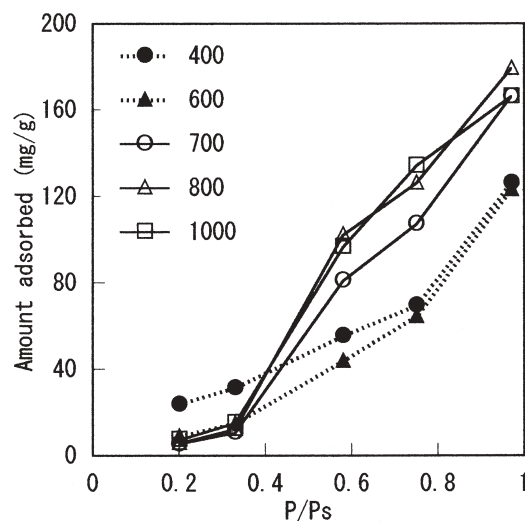
The adsorptivity of carbonized material was evaluated as a value which corresponds to the iodine adsorption number of JIS-K-1474 (activated carbon testing method), i.e., the relationship between the absorbed amount and the carbonizing temperature when  $C$  was 2.5 g/l from the Freundlich equation, which is shown in Fig. 5. The adsorbed amount also decreased as the carbonizing temperature increased in the range 400°–600°C, increased as the temperature increased above 600°C, became a maximum at 800°C, and decreased rapidly at higher temperatures. These trends were similar to those of the  $K$  value.

#### Properties of water vapor adsorption

It is known that charcoal has a humidity control characteristic by which water vapor is adsorbed from a humid atmosphere and desorbed in a dry atmosphere. It is sometimes used as a humidity control material under floors.<sup>12</sup> Abe et al.<sup>11,16</sup> investigated the water vapor adsorption properties of charcoals manufactured under various conditions to deter-



**Fig. 5.** Relationship between amount of adsorbed iodine and carbonizing temperature for waste-paper carbonized materials



**Fig. 6.** Adsorption isotherms of water vapor by waste-paper carbonized materials.  $P/P_s$  is the pressure relative to the saturation pressure of water vapor

mine whether they had a high humidity control capability. However, as for the waste-paper carbonized material, the relationship between the manufacturing conditions and the water vapor adsorption properties has not yet been clarified. Therefore, we measured the water vapor adsorption characteristics of the waste-paper carbonized material prepared at various carbonizing temperatures.

Figure 6 shows the adsorption isotherms of water vapor for the waste-paper carbonized materials. The amount of water-vapor adsorption for waste-paper carbonized material increased as the relative pressure of the water vapor increased. The adsorption behavior was divided into two groups based on the carbonizing temperature. Although the increase in the adsorption amount with the increase in water-vapor relative pressure of the carbonized material

**Table 8.** Adsorption–desorption behavior of water vapor on waste-paper carbonized materials

Carbonized material	Amount of water vapor adsorbed			HCC W2 – W3 W4 (mg/g)
	$P/P_s = 0.05$ W1 (mg/g)	$P/P_s = 0.90$ W2 (mg/g)	$P/P_s = 0.55$ W3 (mg/g)	
400	58	105	67	38
500	47	99	58	41
600	41	110	48	62
700	83	155	97	58
800	105	161	120	41
900	110	157	124	33
1000	108	162	124	38

prepared at 400°–600°C was gradual, the adsorbed amount significantly increased at a relative pressure of 0.4 or more for the waste-paper carbonized material prepared at 700°C or higher. Next, the adsorption–desorption behavior of the water vapor and humidity control capabilities of the waste-paper carbonized material are shown in Table 8. When the water-vapor relative pressure was 0.55, the amount of adsorbed water vapor decreased as the carbonizing temperature increased within the carbonizing temperature range 500°–600°C. The amount of adsorbed water vapor increased as the carbonizing temperature increased to 600°C or higher, and remained almost constant at 800°C or higher. At a relative pressure of 0.90, the amount of adsorbed water vapor could be classified into two groups which were related to a carbonizing temperature between 400° and 600°C and between 700° and 1000°C. The amount of adsorption in each group showed an almost constant value, but the latter group had a higher value. The amount of adsorbed water vapor,  $W_3$ , had higher values than  $W_1$  due to the hysteresis effect.  $W_3$  also increased with a rise in the carbonizing temperature. For  $W_4$ , which is the index of humidity control capability, the carbonized material prepared at 600°C had the highest value. This behavior is almost the same as that of charcoal.<sup>11</sup> With respect to the humidity control capacity, it is thought that the carbonized material prepared at 600°–700°C is the most effective.

## Conclusions

Carbonized materials were prepared from waste newspaper at various carbonizing temperatures, and the changes in the chemical composition, pore structure, and adsorption properties of the carbonized materials were examined. The results are listed below.

1. The yield of carbonized material from the waste paper decreased as the carbonizing temperature increased. However, the decrease in yield due to the increase in the carbonizing temperature was smaller at temperatures greater than 800°C. Moreover, the ratio of carbon in the carbonized material increased as the carbonizing temperature increased.
2. The pH of the carbonized material indicated a weak alkaline condition, with no effect being shown at a carbonizing temperature of 500°C or higher. However, the amount of organic carbon eluted from the carbonized material decreased as the carbonizing temperature increased.
3. The pore distribution for pores with a radius of 100 nm or more, measured by the mercury intrusion porosimetry method, had a peak at approximately 2000 nm for all carbonizing temperatures. Moreover, the pore volume showed a minimum value at a carbonizing temperature of 700°C, and the apparent density reached a maximum value. However, the true density increased as the carbonizing temperature increased.
4. The pore volume and specific surface area measured by nitrogen adsorption indicated maximum values at 800°C and were greater than many commercially available charcoals. However, the carbonized material prepared at 400°–600°C had a remarkably small value.
5. The carbonized material prepared at a carbonizing temperature of 800°C had the highest iodine adsorption number. Moreover, the adsorption rate was low for the material prepared at 400°–600°C, increased for material prepared at 700°C or higher, and was fastest for material prepared at 800°C.
6. The carbonized material prepared at 600°–700°C showed the highest humidity control capacity.

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