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Formaldehyde adsorption by karamatsu (*Larix leptolepis*) bark

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Abstract Formaldehyde adsorption and release tests of karamatsu (*Larix leptolepis*) bark and bark ingredients were performed. Karamatsu bark had good formaldehyde adsorption ability that was better than microcrystalline cellulose. An acetone-soluble fraction from karamatsu bark, which might contain bark tannin, had excellent formaldehyde adsorption ability, and was found to release a trace amount of the adsorbed formaldehyde, suggesting that its formaldehyde adsorption was predominantly due to chemical adsorption. It was confirmed that the acetone-soluble fraction played an important part in formaldehyde adsorption by karamatsu bark. An acetone-insoluble fraction from karamatsu bark had good formaldehyde adsorption ability as well as the bark, in spite of the residue after the removal of the acetone-soluble fraction.

Key words Adsorption · Bark · Bark tannin · Chemical adsorption · Formaldehyde

Introduction

Over the past decade, several reports have emerged concerning the use of bark and bark tannin for formaldehyde (HCHO) adsorption to solve the indoor air-pollution problem of volatile organic compounds.^{1–9} However, a comprehensive study of HCHO adsorption by bark and bark ingredients from the same source is not available. Furthermore, the mechanism of HCHO chemical adsorption by bark has not been proved clearly, although it is supposed that the bark tannin in bark reacts with HCHO vapor. Karamatsu bark is one of the barks reported as a HCHO adsorbent, and HCHO-adsorbing composite or nonwoven fabric

containing karamatsu bark have been proposed.^{5,7,8} This report describes the comparison of the HCHO adsorption abilities of karamatsu bark and bark ingredients and the mechanism of HCHO chemical adsorption by karamatsu bark.

Materials and methods

Materials

Karamatsu (*Larix leptolepis*) whole bark was supplied by Toyama Forestry and Forest Products Research Center. Microcrystalline cellulose (Avicel) and formalin (37% HCHO, 8% methanol; Special grade) were purchased from Merck (Darmstadt, Germany) and Nacalai Tesque (Kyoto, Japan), respectively. The former was ground in a mortar with a pestle and dried in vacuo at room temperature overnight before use. The latter was diluted with distilled water, and HCHO concentration of the dilute solution was determined by the acetylacetone method (JIS A 1460)¹⁰ prior to use. Other chemicals were purchased from Wako (Osaka, Japan) and used without further purification. A Spectra/Pro CE membrane (Spectrum Laboratories, molecular weight cutoff = 500) was used as a dialysis tube.

Preparation of samples for formaldehyde adsorption and release tests

The samples are listed in Table 1. The moisture contents of all samples were determined by the method described in JIS Z 2101.¹¹ Karamatsu bark was milled in a Wiley mill, and sieved to obtain two bark samples (Bark-1, 60–100 mesh; Bark-2, 100 mesh pass). Bark-2 was further ground for 10 min by a cryogenic sample crusher (Model JFC-300, Japan Analytical Industry). The samples were conditioned at 20°C and 60% relative humidity (RH) for 3 days. Furthermore, Bark-1 was dried over P₂O₅ in vacuo at room

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Table 1. Samples for formaldehyde (HCHO) adsorption and release tests

Sample	Particle size (mesh)	Moisture content (%)
Bark-1	60–100	8.0
Bark-2	<100	7.9
Bark-1-LM	60–100	0.9
Bark-1-HM	60–100	10.4
Acetone Soluble-1	60–100	6.4
Acetone Soluble-2	<100	5.6
Acetone Insoluble-1	60–100	7.1
Acetone Insoluble-2	<100	6.2
Cellulose-1	60–100	4.7
Cellulose-2	<100	7.4
Bark-1/AB	60–100	8.2
Acetone Soluble-1/AB	60–100	8.2
Acetone Insoluble-1/AB	60–100	7.2
Cellulose-1/AB	60–100	7.0

LM, Low moisture content; HM, high moisture content; AB, after boric acid treatment

temperature for 7 days and conditioned in the air at room temperature for 3 days to give Bark-1-LM (low moisture content) and Bark-1-HM (high moisture content), respectively. Each bark sample was extracted with ethanol/benzene (1/2, v/v) at 80°C for 4 h using a Soxhlet apparatus. The residue was extracted with 70% acetone aqueous solution at room temperature for 2 h several times, until the solution became colorless, to give an aqueous-acetone-soluble fraction as a brown solid and an aqueous-acetone-insoluble fraction. The samples were ground, sieved, and conditioned by the same method used for bark samples to give Acetone Soluble-1 (or Acetone Soluble-2) and Acetone Insoluble-1 (or Acetone Insoluble-2). Microcrystalline cellulose was sieved and conditioned to afford Cellulose-1 (60–100 mesh) and Cellulose-2 (100 mesh pass) by using the same method used for Bark-1 and Bark-2, respectively.

Boric acid treatment of samples

The suspension of Bark-1 (or Acetone Soluble-1, or Acetone Insoluble-1, or Cellulose-1) in 1.6 mM boric acid solution (sample/boric acid = 50/1, w/w) was stirred at room temperature for 10 min, lyophilized, sieved, and conditioned to give Bark-1/AB (after boric acid treatment) (or Acetone Soluble-1/AB, or Acetone Insoluble-1/AB, or Cellulose-1/AB).

Formaldehyde adsorption test

HCHO adsorption test was performed according to the desiccator method.^{3,4,12} A sample (500 mg) in a petri dish and a filter paper (diameter: 40 mm, No.4, Kiriya-masei-sakusho) dropped with 60 μ l of 2.67 M HCHO solution (160 $\times 10^{-6}$ mol) were put in a desiccator (internal volume: 7.46 l). The desiccator was kept at 20°C. After the prescribed time, HCHO concentration was measured by a detector tube method. A gas sampling pump (GV-100S, Gastec) with a

gas detector tube for HCHO (no. 91 M, measurement range: 8–6400 ppm; 91 L, measurement range: 0.1–40 ppm; Gastec) was used. The test was repeated two or three times.

Formaldehyde release test

Method A

The petri dish containing the test sample in the above HCHO adsorption test was quickly moved to another desiccator after 48 h (internal volume: 5.06 l).⁴ The desiccator was kept at 20°C. After 24 h, HCHO concentration was measured by the detector tube method.

Method B

The petri dish containing the test sample in the above HCHO adsorption test was taken out of the desiccator after 48 h and distilled water (10 ml) was added as soon as possible. The suspension was transferred to a dialysis tube and dialyzed against distilled water (30 ml) at room temperature for 24 h. HCHO concentration of the outer fluid was measured by the acetylacetone method.¹⁰

Preparation of formaldehyde chemically adsorbed samples

Bark-2 (or Acetone Soluble-2) (500 mg) was added to a 300-ml round-bottom flask equipped with a 10-ml Dean-Stark trap, in which formalin (3 ml) was added, according to our method for the reaction of (+)-catechin with HCHO vapor.¹³ The flask was kept at 20°C for 48 h. The HCHO-adsorbed Bark-2 (or Acetone Soluble-2) was dialyzed against distilled water until HCHO in the dialysate was not detected by the acetylacetone method,¹⁰ lyophilized, and dried in vacuo at room temperature for 3 days to give Bark-2-AH (after HCHO treatment) (or Acetone Soluble-2-AH). Bark-2-BH (before HCHO treatment) (or Acetone Soluble-2-BH) was prepared by dialysis treatment without HCHO vapor reaction.

Chemical analyses of formaldehyde chemically adsorbed samples

Bark-2-AH (or Bark-2-BH) was fractionated by the preparation method for Acetone Soluble-1 described above. Bark-2-AH (or Bark-2-BH) and Acetone Soluble-2-AH (or Acetone Soluble-2-BH) were subjected to Fourier transform infrared (FT-IR) diffuse reflectance spectroscopy (DRS) and ¹³C solid-state nuclear magnetic resonance (NMR) measurements. FT-IR spectra were recorded with a Shimadzu FTIR-8600 spectrophotometer equipped with a Shimadzu DRS-8000 attachment. ¹³C Solid-state NMR spectra were recorded with a Jeol CMX300 FT-NMR (300 MHz) spectrometer.

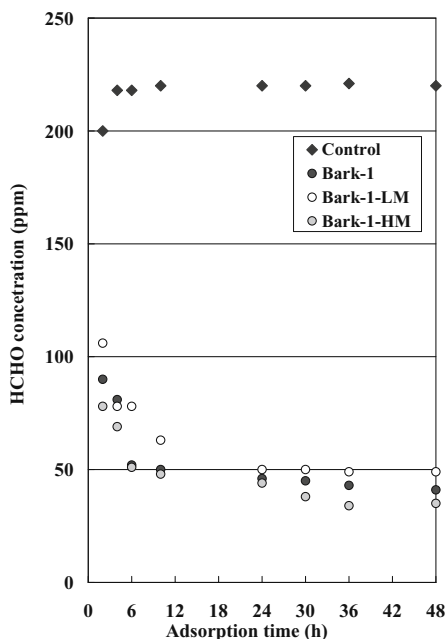


Fig. 1. Results of formaldehyde (HCHO) adsorption tests of Bark-1 samples with different moisture contents. *LM*, Low moisture content; *HM*, high moisture content

Results and discussion

Preliminary experiment for the formaldehyde adsorption test

The desiccator method is widely used as a HCHO adsorption test.^{3,4,12} First, the HCHO adsorption test was performed without a sample as a control experiment, because the time required to reach a steady concentration of HCHO in the desiccator by release of HCHO from the filter paper was unknown. The results are shown in Fig. 1. It was found that HCHO concentration in the desiccator became constant (220 ppm) after 10 h.

Influence of moisture content of karamatsu bark sample on formaldehyde adsorption

It is reasonable to expect that the moisture content of Bark-1 might influence its HCHO adsorption ability, because water is a very good HCHO adsorbent. The results of HCHO adsorption tests of bark samples (Bark-1, Bark-1-LM, Bark-1-HM) with different moisture contents and same sizes are shown in Fig. 1. In all cases, HCHO concentration decreased rapidly within 10 h, then declined slightly, and leveled off at 48 h, although we have to consider that HCHO concentration was not at equilibrium until 10 h had passed. HCHO concentrations at 48 h for Bark-1, Bark-1-LM, and Bark-1-HM were 41, 49, and 35 ppm, respectively, suggesting that attention be paid to the moisture content of bark samples in evaluation of HCHO adsorption ability.

Formaldehyde adsorptions of karamatsu bark and bark ingredient samples

Bark-1 (or Bark-2) was extracted with ethanol/benzene and subsequently fractionated with 70% acetone aqueous solution, which is a typical extraction for condensed tannins, to afford a 70% acetone-soluble fraction [Acetone Soluble-1 (or Acetone Soluble-2)] and a 70% acetone-insoluble fraction [Acetone Insoluble-1 (or Acetone Insoluble-2)]. Microcrystalline cellulose was also used as a control sample. The results of HCHO adsorption tests for the two series of samples, sample-1 with 60–100 mesh size (Bark-1, Acetone Soluble-1, Acetone Insoluble-1, and Cellulose-1) and sample-2 with 100 mesh pass (Bark-2, Acetone Soluble-2, Acetone Insoluble-2, and Cellulose-2), are shown in Fig. 2.

Bark-1 and Bark-2 had good HCHO adsorption abilities and adsorbed HCHO better than Cellulose-1 and Cellulose-2, respectively. HCHO concentrations at 48 h for Bark-1 and Bark-2 were 41 and 38 ppm, respectively, suggesting that the influence of particle size of the bark sample on HCHO adsorption was relatively small. Acetone Soluble-1 and Acetone Soluble-2, which might be bark tannin, had excellent HCHO adsorption abilities. These results are in agreement with other reports concerning HCHO adsorption by bark tannin.^{1,3,4,8} However, there was a remarkable difference between Acetone Soluble-1 and Acetone Soluble-2; that is, HCHO concentrations at 48 h for Acetone Soluble-1 and Acetone Soluble-2 were 30 and 1 ppm, respectively, showing that the HCHO adsorption of acetone-soluble samples was greatly influenced by the sample particle size. Unexpectedly, Acetone Insoluble-1 showed good HCHO adsorption ability as well as Bark-1, in spite of the residue after removal of the 70% acetone-soluble fraction. A similar tendency was found in HCHO adsorption by Acetone Insoluble-2. The influences of sample particle size of acetone-insoluble samples on HCHO adsorption were also similar to those of bark samples. These may be due to the formation of a porous structure by the extraction or contribution of polyphenol components in Acetone Insoluble-1 (or Acetone Insoluble-2), which were not extracted with ethanol/benzene or 70% aqueous acetone solution, such as condensed tannins with high molecular weight and lignin. These results suggest that Acetone Insoluble-1 (or Acetone Insoluble-2) is also useful as a HCHO adsorbent.

Formaldehyde release from karamatsu bark and bark ingredient samples

The HCHO release test (method A) was performed by a modified method of Ohara,⁴ in which HCHO concentration was measured after 72 h. In this study, HCHO concentration was measured after 24 h, because the preliminary experiment using HCHO-adsorbed Bark-1 showed that HCHO concentration in the desiccator attained equilibrium after 6 h (data not shown). The HCHO release test (method B) was newly designed to understand HCHO chemical

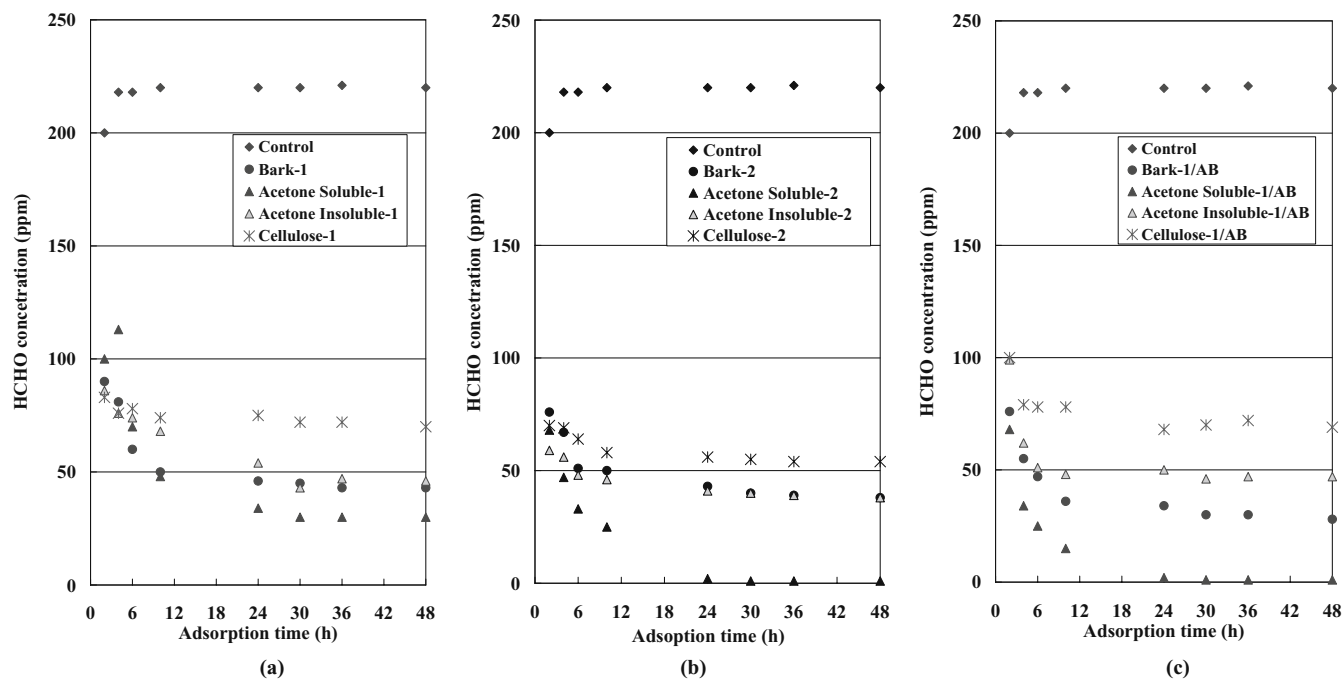


Fig. 2a–c. Results of HCHO adsorption tests of **a** samples-1 (60–100 mesh), **b** samples-2 (100 mesh pass), and **c** samples-1 after boric acid treatment (AB)

Table 2. Results of HCHO release tests

Sample	HCHO released ($\times 10^{-6}$ M)	
	Method A	Method B
Bark-1	0.6	20.5
Acetone Soluble-1	0.4	3.8
Acetone Insoluble-1	4.2	24.1
Cellulose-1	7.6	26.4

adsorption of the samples. HCHO concentration was measured after 24 h, because HCHO concentration in the outer fluid leveled off after 12 h in the test of HCHO-adsorbed Bark-1 (data not shown). The results of HCHO release tests are shown in Table 2.

The amount of HCHO released from Bark-1 by method A was much less than that revealed by method B. Similar results were obtained in the HCHO release test of Acetone Insoluble-1 and Cellulose-1. These results suggest that method A is inadequate to evaluate HCHO chemical adsorption of the samples, although it is suitable for evaluation of HCHO released in the practical use of the samples as HCHO adsorbents. In the method B test, the amount of HCHO released from Bark-1 was lower than that from Cellulose-1, suggesting that Bark-1 adsorbed HCHO chemically, to some degree, more than Cellulose-1. The amount of HCHO released from Acetone Soluble-1 was significantly small, even by method B, suggesting that HCHO adsorption by Acetone Soluble-1 was predominantly due to chemical adsorption. The amount of HCHO released from Acetone Insoluble-1 was a little higher than that from Bark-1. This can be explained in terms of the influence of the removal of the 70% acetone-soluble fraction of Bark-1.

Table 3. Results of fractionation of Bark-2-AH and Bark-2-BH

Sample	Yield (%)	
	Ethanol/benzene extract	70% Acetone extract
Bark-2-AH	4.9	4.9
Bark-2-BH	4.2	14.7

AH, After formaldehyde treatment; BH, before formaldehyde treatment

These results suggest that Acetone Soluble-1 played a part in the HCHO chemical adsorption of Bark-1.

Formaldehyde chemical adsorption of karamatsu bark sample

Bark-2-AH was prepared from Bark-2 by the modified method for the HCHO adsorption and release tests to clarify the mechanism of HCHO chemical adsorption of the bark sample. This was because a small sample with an adequate amount of adsorbed HCHO was preferable to chemical analyses. Bark-2-BH was also prepared as a blank sample. Bark-2-AH and Bark-2-BH were subjected to FT-IR DRS and ^{13}C solid-state NMR measurements. However, a clear difference was not observed in their spectra, suggesting that a trace amount of HCHO was adsorbed chemically on the surface of Bark-2. Bark-2-AH and Bark-2-BH were fractionated by ethanol/benzene extraction and by the subsequent extraction with 70% aqueous acetone solution. The yields of the soluble fractions are listed in Table 3. The yields of ethanol/benzene-soluble fractions of Bark-2-AH and Bark-2-BH were approximately the same, whereas the

yield of the 70% acetone-soluble fraction of Bark-2-AH was significantly lower than that of Bark-2-BH, indicating that HCHO reacted with the 70% acetone-soluble fraction in Bark-2. These results were in good agreement with the results for Bark-1 and Acetone Soluble-1 in the HCHO release test.

Formaldehyde chemical adsorption of acetone-soluble sample

Acetone Soluble-2-AH and Acetone Soluble-2-BH were prepared and subjected to FT-IR DRS measurements. A small increase of a broad band in the range of 850 to 1050 cm^{-1} , which might be caused by the bands derived from methylene group (910 cm^{-1}) and from methylol group (1010 cm^{-1}),¹⁴ was found in the difference spectrum between them, although clear information concerning the chemical structure of Acetone Soluble-2-AH could not be obtained. On the other hand, we have reported that the reaction of (+)-catechin with HCHO vapor without a solvent and a catalyst proceeded via an aldol-condensation-type reaction (methylolation, condensation, and polymerization) to afford a (+)-catechin polymer.¹³ Therefore, it is supposed that HCHO chemical adsorptions of acetone-soluble samples were caused by such aldol-condensation-type reactions between the A-ring of bark tannin and HCHO.

Influence of boric acid treatment of karamatsu bark and bark ingredient samples on formaldehyde adsorption

If the aldol-condensation-type reaction occurs in HCHO chemical adsorption of bark and acetone-soluble samples, HCHO adsorption is expected to be assisted by an acid.¹⁵ A HCHO adsorption test of a mixture of the sample and boric acid was carried out. The results are shown in Fig. 2c. HCHO adsorption abilities of Bark-1/AB and Acetone Soluble-1/AB were higher than those of Bark-1 and Acetone Soluble-1, respectively. HCHO adsorption abilities of Acetone Insoluble-1 and Cellulose-1 were not enhanced by the boric acid treatment. These results suggest that the aldol-condensation-type reaction of the acetone-soluble fraction in bark, which might be bark tannin, was one of the mechanisms of HCHO chemical adsorption by the bark sample. It was also found that mixing of a catalyst of an aldol condensation such as silica, silicic acid, or boric acid was useful to enhance HCHO chemical adsorption by bark and bark tannin.

Conclusions

Karamatsu bark and acetone-soluble samples, which might contain bark tannin, had good HCHO adsorption abilities

as reported to date.¹⁻⁹ Unexpectedly, acetone-insoluble samples were also useful as HCHO adsorbents. This result is important from the viewpoint of whole use of the bark. It was confirmed that acetone-soluble fractions played an important part in HCHO chemical adsorption by karamatsu bark, and that the aldol-condensation-type reaction was responsible for HCHO chemical adsorption by Karamatsu bark.

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