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ORIGINAL ARTICLE

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Preparation of activated carbon moldings from the mixture of waste newspaper and isolated lignins: mechanical strength of thin sheet and adsorption property

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Abstract To expand the utilization of waste newspapers and lignin, activated carbon (AC) sheets, as an example of AC moldings, were prepared from those mixtures. The isolated lignins used were softwood and hardwood acetic acid lignins (SAL and HAL), softwood kraft lignin (KL), and wheat-straw lignin (WSL). The mixtures were molded into precursory sheets by thermal compression and then converted to AC sheets by carbonization and steam activation. The flexural strength of the precursory sheets was dramatically improved by additing the lignins compared to that of sheets without lignin. The strength of several sheets was more than 25 MPa. This suggested that lignins act as adhesives. SAL and HAL sheets with 40% newspaper were strengthened by the carbonization, whereas the strength of other lignin sheets was depressed. Finally, the AL-based AC sheets showed higher flexural strength (>6 MPa) than others. Most of the AC sheets had adsorption ability comparable to that of commercially available AC powder and granules. The capacities were almost independent of paper content. Among the AC moldings tested, the AL-based AC sheets showed the fastest adsorption to *p*-chlorophenol. Thus, viable AC moldings can be prepared from lignin–wastepaper mixtures, particularly SAL and HAL.

Key words Activated carbon moldings · Adsorption · Isolated lignin · Mechanical strength · Fiberboard

Introduction

To establish a total utilization system of woody biomass components, we have developed atmospheric acetic acid pulping for separating the components. One of the uses of the lignin (acetic acid lignin, or AL) isolated by the pulping is in AL-based activated carbon (AC) moldings, such as AC fibers and sheets; and we reported on their preparation and adsorption properties elsewhere.[1-3] During the preparation of AC sheets from only AL, however, there was a big problem: deformation of the AL sheets during carbonization. The morphological change was diminished by adding cellulosic materials, such as rayon and acetic acid pulp, to AL in small quantities. The deformation was completely repressed by a 10% addition of the pulp.[3] However, we did not investigate either the mechanical properties or the effect of larger pulp contents on the adsorption ability.

In this study, disintegrated waste newspaper was used as the cellulosic materials from the viewpoint of reusing the wastepapers. Softwood kraft lignin (KL) and wheat-straw lignin (WSL) as by-products of conventional pulping of softwood and wheat straw, respectively, in addition to the ALs were applied to the sheet preparation. Precursory sheets for AC sheets were prepared by varying the paper content from 20% to 100%, and the flexural strength of the resulting sheets was measured. For large-scale production of AC sheets, carbonization and steam activation were performed in a larger electric furnace (24 l) than the furnace previously reported.[1-3] Previously we had adopted the carbonization method that was practiced under a stream of nitrogen, but this time it was attempted under reduced pressure so much more nitrogen could be introduced. This method was expected to reduce the production cost of AC moldings.

In this article, we report the preparation of thin AC sheets from a 10-g mixture of the isolated lignins and waste newspaper and the adsorption properties of the resulting AC sheet. We also examined the adsorption behavior of the AC sheets against *p*-chlorophenol as one of the toxic chlorinated organics.

Materials and methods

The SAL and HAL were prepared by atmospheric acetic acid pulping of todo fir[4] and birch chips.[5] KL was commercially available, with the trade name Indulin AT. WSL was

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Table 1. Dimensions of precursory sheets

Pulp content (%)	Thickness[a] (mm)	Density (g/cm^3)
SAL		
20	1.07 (0.04)	1.19
40	1.40 (0.05)	0.91
60	1.32 (0.08)	0.96
80	1.31 (0.03)	0.97
HAL		
20	1.15 (0.12)	1.11
40	1.28 (0.08)	0.99
60	1.27 (0.07)	1.00
80	1.29 (0.06)	0.99
KL		
40	0.97 (0.07)	1.32
60	0.99 (0.03)	1.29
80	1.22 (0.05)	1.04
WSL		
20	0.93 (0.02)	1.37
40	1.03 (0.06)	1.24
60	1.16 (0.07)	1.10
80	1.22 (0.03)	1.04
Pulp		
100	1.44 (0.04)	0.88

The sheets were 10cm in diameter and weighted 10g
SAL/HAL, softwood/hardwood acetic acid lignans; KL, softwood kraft lignan; WSL, wheat-straw lignan
[a] Values are the average of seven sheets; numbers in parentheses are standard deviations

prepared by soda cooking of wheat straw and was kindly supplied by K-L. Chen, Yunnan Industrial University.

Precursory sheets were prepared from a mixture of lignins and waste newspaper using the thermal compression method, as follows. The waste newspaper was disintegrated and air-dried to give pulp. The pulp was mixed with lignins in the range of 20%–100% pulp by a domestic mixer. The mixture (10g) was placed in a cylindrical stainless steel vessel with a diameter of 10cm and then was molded to a sheet by thermal pressure under 60kg·cm^{-2} at the glass transition temperature (T_g) of lignins used for 10min in a similar manner for preparing a pellet for infrared (IR) measurement. The dimensions and density of the resulting precursory sheets are shown in Table 1.

The sheets were thermostabilized for 1h at 250°C in air at a heating rate of 2°C/min from room temperature.[1] They were then carbonized at 1000°C for 1h under reduced pressure at a heating rate of 180°C/h. The carbonized sheet was activated with steam at 900°C for 2h in a 24-l electric furnace to yield the AC sheet. Steam was introduced into the furnace with an N_2 stream at a flow rate of 1l/min, as described previously.[6] The steam/N_2 volume ratio was approximately 50%.[3]

The precursory, carbonized, and AC sheets were cut into small squares (width 1cm) and then subjected to a measurement of flexural strength according to Japan Industrial Standard (JIS K 6911). In the case of precursory sheets, water absorptivity (WA) was measured by the following equation after immersing the sheets in water for 30 days.

$$\mathrm{WA}\,(\%) = (m_2 - m_1)/m_1 \times 100$$

where m_1 is the mass of the oven-dried sheet, which was weighed after immersion and drying; and m_2 is the mass of the sheet after immersion. During immersion, the sheet thickness was monitored every day.

Adsorption capacities of AC sheets against iodine (I_2) and methylene blue (MB) were measured after milling the sheets in accordance with JIS K 1474. The mesh of the powder was not adjusted.

The adsorption rate of *p*-chlorophenol onto the AC sheet was estimated by its residual concentration. A portion of the AC sheet (0.1g) was immersed in 100ml of *p*-chlorophenol (0.1mol·l^{-1}) with gentle stirring at room temperature. The concentration of the solution was determined by the fluorescence intensity at the emission of 612nm (excitation 281nm) at certain time intervals.

Results and discussion

Characteristics of precursory sheets

A mixture of lignin preparations and waste newspaper pulp were used as raw materials for the precursory AC sheets. Although the mixture could be molded into a sheet by pressure at ambient temperature, the sheet was prepared by thermal compression at T_g of the lignins of 125°–128°C for the ALs, 180°C for KL, and 170°C for WSL. The T_g was evaluated by thermomechanical analysis.[7] Thermal compression was used because of an expectation that the lignins would be highly miscible with fibrous material after thermal softening of the lignins. However, HAL- and SAL-based mixtures could be molded in the molten state of lignins at higher temperatures because of the complete and partial fusibility of the lignins, respectively. The effect of the compression temperature on the mechanical strength is under investigation.

Figure 1 shows the flexural strength of the precursory sheet obtained versus the pulp content. Although the strength of the 100% pulp sheet was less than 5MPa, it was dramatically improved by the addition of each of the lignins. In the series of both AL sheets, 80% pulp sheets indicated maximal strength of more than 25MPa. The value of the KL sheets with 60% pulp reached about 30MPa. Among the sheets tested, the WSL sheet with 40% pulp showed the highest strength (35MPa). The specific gravities of these sheets were more than 1g/cm^3. Therefore, it was found that such lignin-mixed sheets fulfilled the strength of S 25 hardboard noted in JIS A 5905.

The ability of the sheets to gain water was evaluated, because JIS noted moisture content as one of the quality items. In this study, the moisture content was measured after immersing the sheets in water for 30 days. As expected, the 100% pulp sheet absorbed much water [water absorptivity (WA) 220%], as shown in Fig. 2. The WA was decreased by the increase in lignin content. The SAL sheet with 20% pulp showed the lowest WA (<25%). Furthermore, all the sheets were markedly expanded after 1 day of immersion, and then the expansion was gradual, as depicted in Fig. 3, where the thickness change is shown. However, the expansion of all 20% pulp sheets was small. It was

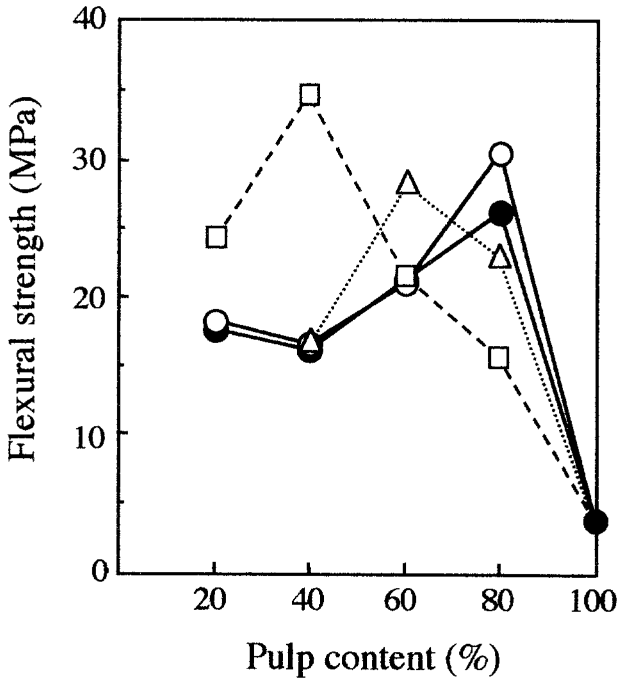

Fig. 1. Flexural strength of precursory sheets. *Open circles*, hardwood acetic acid lignans (HAL); *filled circles*, softwood acetic acid lignans (SAL); *triangles*, softwood kraft lignin (KL); *squares*, wheat-straw lignin (WSL)

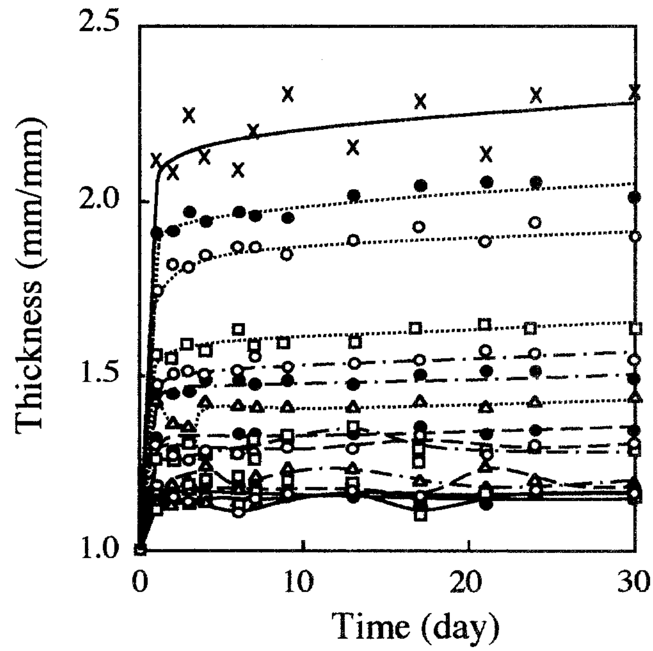

Fig. 3. Changes in thickness during 30 days of immersion in water. *Solid lines*, 20% pulp sheet; *broken lines*, 40% pulp sheet; *dashed lines*, 60% pulp sheet; *dotted lines*, 80% pulp sheet; *crosses*, 100% pulp sheet; *open circles*, HAL; *filled circles*, SAL; *triangles*, KL; *squares*, WSL

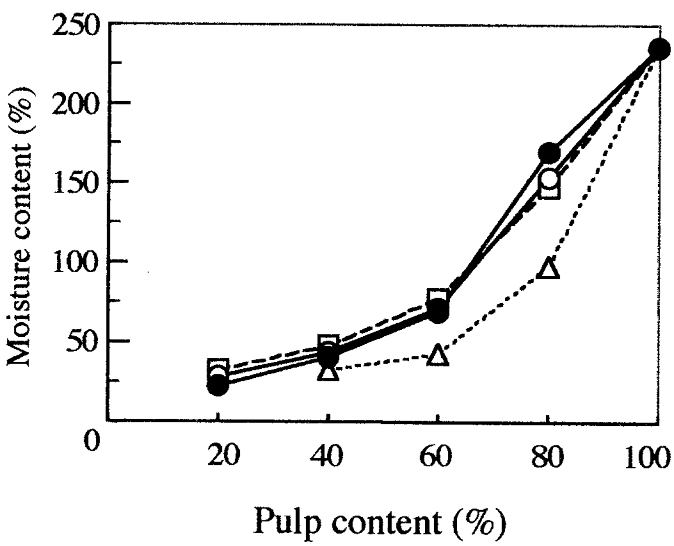

Fig. 2. Water absorptivity of precursory sheets after 30 days of immersion in water. *Open circles*, HAL; *filled circles*, SAL; *triangles*, KL; *squares*, WSL

apparent that any added lignin made the sheet water-repellent. The WA ability of the SAL sheet passes the test of water absorption noted in JIS, but the flexural strength was less than the value of S25. To utilize such lignin-mixed sheets as fiberboard, strengthening the sheet is under investigation. However, the strength was enough for the precursory sheet in terms of handling it for additional treatments.

Carbonization of the precursory sheets

Although the SAL sheet could be converted to a carbonaceous sheet by direct carbonization without thermostabilization,[3] the lignin-based sheets prepared in this study were converted after thermostabilization because the HAL sheet even with cellulosic materials was deformed during carbonization owing to the fusible characteristic of HAL. Figure 4 shows the flexural strength of carbonized sheets. The strength profiles versus the pulp content in Fig. 4 were quite different from those in Fig. 1. The strength of KL- and WSL-based carbonized sheets in the whole range of pulp contents was markedly decreased by carbonization. On the other hand, both HAL- and SAL-based carbonized sheets derived from 40% pulp sheets were strengthened where the values were higher than 25 MPa. The strength of AL-based carbonized sheets depended on the lignin content. Such a specific feature of the AL sheet might be attributed to its developing a carbon structure, such as a graphite structure. Molecular fusion for forming the large carbon crystallite would easily occur in AL sheets, as ALs are more thermally active than other lignin preparations.

Characteristics of AC sheets

The carbonized sheets were converted to AC sheets by steam activation in a large furnace. It was found in the preliminary experiment that the efficiency of steam activation in the furnace depended on the activation time at 900°C but not on the flow rate of steam. Based on previous data,[3] the activation was performed for 2 h.

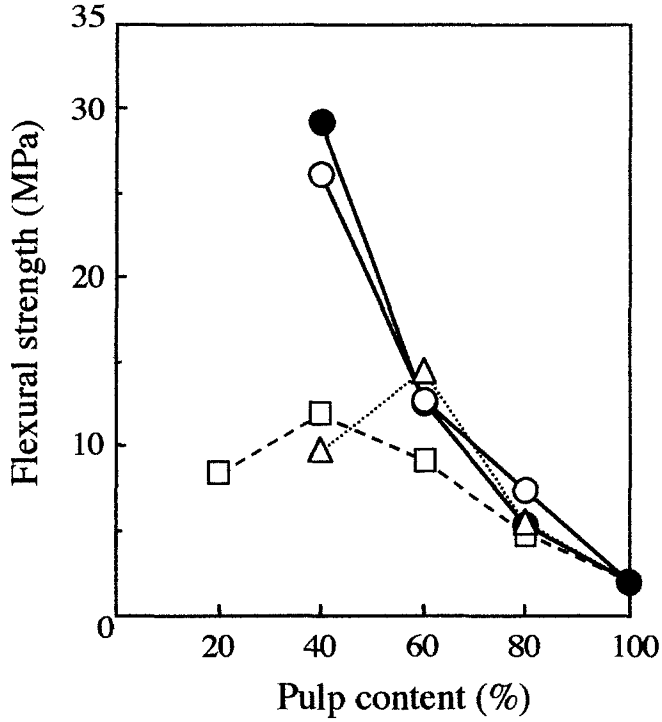

Fig. 4. Flexural strength of carbonized sheets. *Open circles*, HAL; *filled circles*, SAL; *triangles*, KL; *squares*, WSL

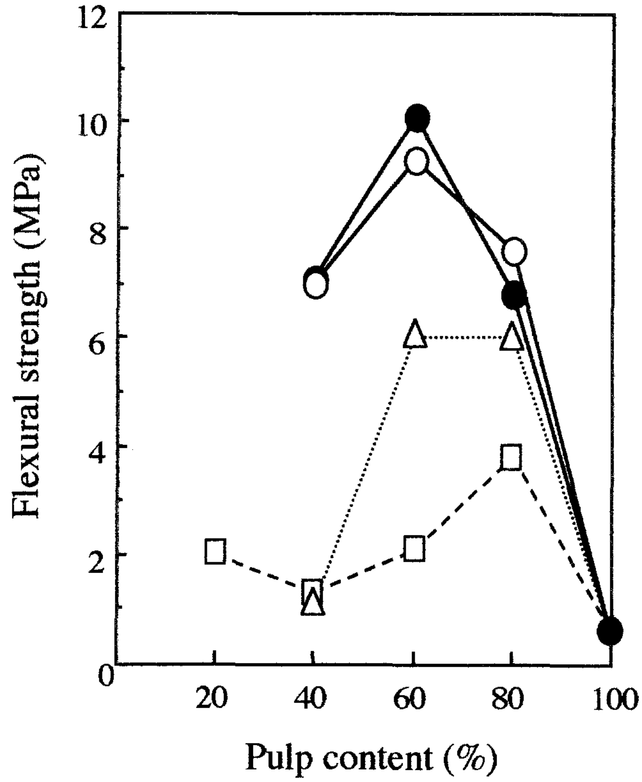

Fig. 5. Flexural strength of activated carbon sheets. *Open circles*, HAL; *filled circles*, SAL; *triangles*, KL; *squares*, WSL

As expected, the flexural strength of all AC sheets was decreased by the activation compared with that of the corresponding carbonized sheets, because the process created many small pores in the sheets that acted as a defect in the strength. A series of WSL-based AC sheets were extremely weak, as shown in Fig. 5. By contrast, the decline in the strength of the AL-based sheets was small. Both HAL- and SAL-based AC sheets with 60% pulp showed maximal strength; particularly, the SAL-based AC sheets had 10MPa of strength. Thus, AL sheets were promising precursory sheets for producing AC sheets with respect to flexural strength.

In the previous report,[3] we assumed that cellulosic material in AC sheets would act as fibrous AC. The influence of the pulp content on the adsorption ability of AC sheets was investigated concerning the production yields of AC sheets because the adsorption ability of AC, in general, was closely related to AC yields. Figures 6 and 7 show the overall yield of AC sheets and the I_2 and MB adsorption capacities versus the pulp content, respectively. We did not measure the specific surface area because the Langmuir surface area could be deduced from the I_2 adsorption capacity.[3] The yields of SAL- and HAL-based AC sheets decreased with increasing pulp content, whereas such dependence was not observed for KL- and WSL-based AC sheets; they had maximal yields at 40% pulp. Consequently, there seemed be no simple relation between the yield and the pulp content. Similarly, no linear relation between the pulp content and adsorption capacities was observed; although, strictly speaking, there was little dependence of the adsorption capacity on the pulp content for individual lignin sheets (as discussed in the next paragraph). Therefore, the adsorption ability AC sheets with more pulp prepared under uniform

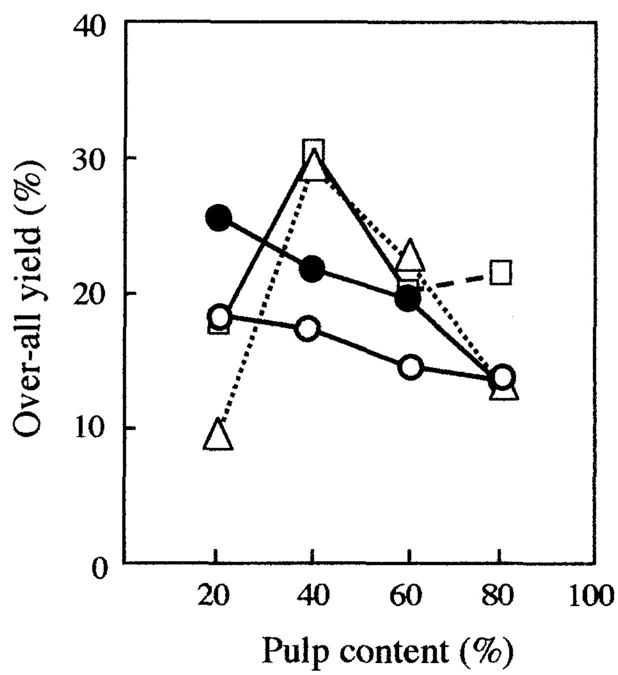

Fig. 6. Overall yield of AC sheets. *Open circles*, HAL; *filled circles*, SAL; *triangles*, KL; *squares*, WSL

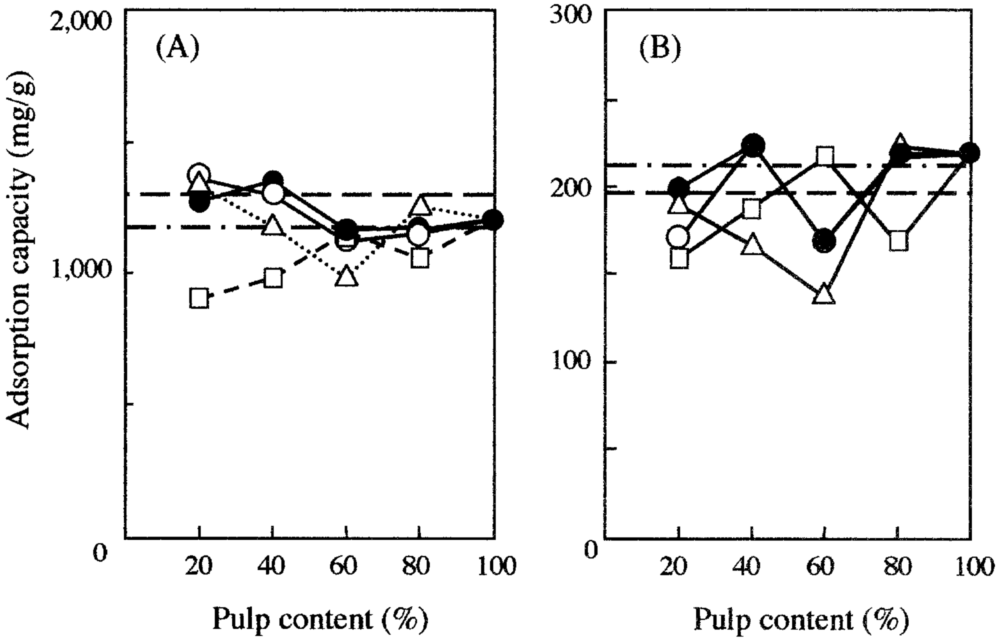

Fig. 7. Iodine (**A**) and methylene blue (**B**) adsorption capacities of activated carbon sheets. *Open circles*, HAL; *filled circles*, SAL; *triangles*, KL; *squares*, WSL

activation conditions did not depend mainly on the yield or pulp content, although adsorption might be affected by the nature of the lignin preparations.

The I_2 and MB adsorption capacities of both HAL- and SAL-based AC sheets indicated high values for the entire range of pulp contents, except for 60% pulp sheets, which were comparable to commercial AC powder and granules. The inferior adsorption ability at a pulp content of 60% indicates that the activation proceeded insufficiently compared with other pulp contents. Therefore, both AL-based AC sheets with 60% pulp content showed the highest strength, as described above. Probably it can be attributed to the rigid complex formation of both ALs and the pulp. By contrast, the I_2 adsorption capacity of the WSL-AC sheet significantly depended on the pulp content but was lower than those of AL-AC sheets. In addition, the I_2 and MB adsorption capacities of the KL-based AC sheets were decreased with increases in pulp content up to 60%. The following lignin property as a raw material for AC was deduced from those results. Both ALs were excellent raw materials for AC because of their superior ability to adsorb as AC fibers.[1,2] Taking the formation of a rigid carbonized sheet from a mixture of the two ALs and the wastepaper into consideration, they would act cooperatively as adsorbents. WSL is unsuitable raw material for AC sheets because the adsorption capacity of the WSL-based AC sheet with low pulp content (20%) is low. Accordingly, the adsorption ability of the WSL-AC sheets was due to the pulp component of fibrous AC. KL appeared to be a good resource for AC, although its adsorption ability was reduced by the addition of pulp, probably due to the immiscibility of KL with pulp. Thus, the performance of lignin-based AC sheets relates to the potential of lignin preparations for the AC substrate.

We further investigated the adsorption property of AC sheets to evaluate their viability as an adsorbent for toxic organic compounds. The adsorption rate of p-chlorophenol onto the sheets with 40% pulp is depicted in Fig. 8. In general, the adsorption rate of AC molding (e.g., granules) is slower than that of AC powder, as observed in this experiment. This phenomenon is likely to be attributed to the area of adsorbent accessible to the adsorbates. The p-chlorophenol adsorption of HAL- and SAL-based AC sheets was much faster than commercial AC granules despite the larger molding. As conjectured from the low I_2 and MB adsorption of the WSL-based AC sheet, the adsorption onto it proceeded slowly, and the adsorption capacity was the lowest among the sheets tested. Therefore, the AL-based AC sheet had the best adsorption properties in terms

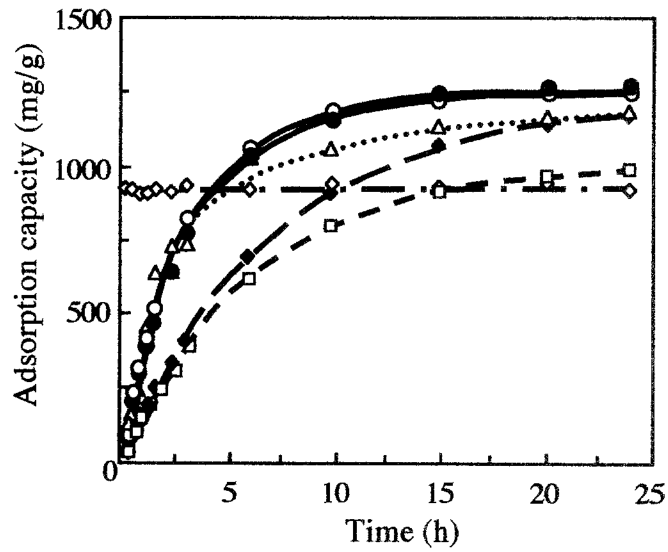

Fig. 8. Adsorption rate of p-chlorophenol onto activated carbon sheets. *Open circles*, HAL; *filled circles*, SAL; *triangles*, KL; *squares*, WSL

of strength and the adsorption capacity and rate. It is concluded that HAL and SAL were the most promising lignins for use as adhesives for cellulosic materials and a resource for AC.

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