Characteristics of Adsorption of Organic Solvent Vapors by a New Porous Carbon Material Made of Rice Husk as Measured by Breakthrough Curves

Mitsuo Hinoue*, Kunio Hara and Hajime Hori

Department of Occupational Hygiene, School of Health Sciences, University of Occupational and Environmental Health, Japan. Yahatanishi-ku, Kitakyushu 807-8555, Japan

Abstract: We investigated the adsorbed amount of organic solvent vapors and adsorption rate of a new porous carbon material made from rice husk (rice husk activated carbon) in comparison with those of coconut shell activated carbon by the breakthrough curve. The adsorbed amount on the rice husk activated carbon and that on the coconut shell activated carbon were 81.3 ± 3.3 mg/g and 71.7 ± 5.0 mg/g for acetone, 8.0 ± 1.7 mg/g and 6.3 ± 0.2 mg/g for methanol, 196.8 ± 8.8 mg/g and 262.8 ± 10.4 mg/g for ethyl acetate, 234.8 ± 11.9 mg/g, and 364.6 ± 43.8 mg/g for toluene, respectively. These results suggest that the amount of organic solvent vapors adsorbed per unit weight of rice husk activated carbon is slightly larger for high polar compounds and is smaller for low polar compounds than that of coconut shell activated carbon. We compared the adsorption rate of the two materials by using the slope of the breakthrough curves. Even though there are some limitations to the characteristics of the new porous carbon material, it may be possible to use rice husk activated carbon as an alternative to coconut shell activated carbon in occupational and environmental measures.

Keywords: new porous carbon material, rice husk, breakthrough curve, organic solvent, adsorption amount.

Introduction

Many organic solvents are used in the workplace, and it is important to prevent the exposure of organic solvent vapors to workers because they induce adverse effects on humans. Measures to control exposure include the use of local exhaust ventilation systems and respiratory protective equipment. Coconut shell activated carbon is commonly used in respirator cartridges and canisters for organic vapors. Activated carbon is also used in the solid adsorption method for measuring organic solvent vapors in the working environment [1, 2], and in air purifier filters, water purifier cartridges, and refrigerator deodorizers in houses and residences.

Activated carbon, which is manufactured mainly from wood, coal, and petroleum, has a large specific surface area because of the many pores on its surface (porous structure) and can adsorb large amounts of organic solvent vapors. Ordinary coconut shell activated carbon, which is mainly used in respirator cartridges and canisters, has a large adsorption capacity for substances with low polarity, such as toluene, but has a very low adsorption capacity for substances with high polarity, such as methanol [3]. A material that has more adsorption capacity for substances with high polarity than ordinary coconut shell activated carbon would be highly useful.

A new porous carbon material made of rice husk...
was developed recently. Its characteristics are different from those of ordinary activated carbon because rice husk has a high silica content (about 20%), micropores (< 2 nm), many mesopores (2-50 nm), and many macropores (> 50 nm), and its density is about 60% smaller than that of coconut shell activated carbon [4].

The porous carbon material focused on in this study is made from rice husk by a new method, hereinafter referred to as rice husk activated carbon. Rice husk is a huge waste material in many countries, including Japan. If the characteristics of this porous carbon material are preferable in terms of environmental and occupational factors, it can be a new, alternative use of rice husk.

There is little basic data on the adsorption of organic solvent vapors such as toluene on the porous carbon material, although the characteristics of ammonia and an aerosol containing virus adsorption have been examined [4]. We conducted an adsorption study to compare rice husk activated carbon and coconut shell activated carbon, a common type of activated carbon, in the adsorbed amounts and adsorption rates of organic solvent vapors that are widely used in the workplace, including high polar and low polar substances.

Methods

Experimental equipment

A schematic diagram of the experimental setup is shown in Figure 1.

N2 gas containing organic solvent vapors was prepared in a 10 l Tedlar bag (4) placed in a cool incubator (3) at 25°C to maintain a constant temperature. Adsorption was carried out in an adsorption cell (5) placed in a small cool incubator (6). The adsorption cell used was a PFA tube with an inner diameter of 6 mm and a length of 20 mm, and it was packed with the same volumes of activated carbon. The weight of the packed carbon was about 130 mg for the rice husk activated carbon (Triporous, Sony Group Corporation) and 220 mg for the coconut shell activated carbon. The air flow rate was 245 ml/min. A gas chromatograph equipped with a flame ionization detector (FID) (GC-17A, SHIMADZU) (8) was used to determine the concentration of the organic solvent vapors. The temperatures of the injection port, detector, and column oven were 200°C, 220°C and 60-80°C, respectively.

The rice husk activated carbon and the coconut shell activated carbon (KGC-1 type L for organic gases, Ko-ken) were sieved in the range of 1.0 to 1.4 mm, and dried at 110°C for about 3 hours before use. The organic solvents used were acetone, methanol, ethyl acetate and toluene.

Calculation of adsorption volume [5]

A breakthrough curve was obtained from the results of the adsorption experiment. The weight of organic solvent adsorbed in the activated carbon (mg) was calculated from the breakthrough curve and an inlet vapor concentration by using graphical integration.

Estimation of adsorption rate

The slope of the breakthrough curve was determined at concentrations ranging from about 15 to 85% of the prepared concentration to compare the adsorption rate between rice husk activated carbon and coconut shell activated carbon.

Statistical tests

Paired t-test was used for statistical analysis on adsorption capacity and adsorption rate between the two types of adsorbents.

Results

The breakthrough curves of acetone, methanol, ethyl acetate, and toluene on the rice husk activated carbon and the coconut shell activated carbon are shown in
Figures 2–5. The amounts of each organic solvent adsorbed per unit weight of activated carbon were calculated from these breakthrough curves, and are shown in Table 1. The table shows that the amounts of each organic solvent adsorbed in the rice husk activated carbon were 81.3 ± 3.3 mg/g for acetone, 8.0 ± 1.7 mg/g for methanol, 196.8 ± 8.8 mg/g for ethyl acetate, and 234.8 ± 11.9 mg/g for toluene; and those in the coco-
The slopes of the breakthrough curves are summarized in Table 2. The slopes obtained by the rice husk activated carbon were 0.40 ± 0.02 mg/(g·min) for acetone, 0.25 ± 0.06 mg/(g·min) for methanol, 0.59 ± 0.07 mg/(g·min) for ethyl acetate, and 0.78 ± 0.07 mg/(g·min) for toluene; and those by the coconut shell activated carbon were 0.24 ± 0.01 mg/(g·min) for acetone, 0.11 ± 0.01 mg/(g·min) for methanol, 0.28 ± 0.04 mg/(g·min) for ethyl acetate, and 0.43 ± 0.03 mg/(g·min) for toluene.

Table 1. The amount of organic solvent vapors adsorbed to the adsorbent

| Materials                     | Acetone mg / g | Methanol mg / g | Ethyl acetate mg / g | Toluene mg / g |
|-------------------------------|----------------|-----------------|----------------------|---------------|
| Rice husk activated carbon    | 81.3 ± 3.3     | 8.0 ± 1.7       | 196.8 ± 8.8          | 234.8 ± 11.9  |
| Coconut shell activated carbon| 71.7 ± 5.0     | 6.3 ± 0.2       | 262.8 ± 10.4         | 364.6 ± 43.8  |

Table 2. The rate of organic solvent vapors adsorbed to the adsorbent

| Materials                     | Acetone mg / (g·min) | Methanol mg / (g·min) | Ethyl acetate mg / (g·min) | Toluene mg / (g·min) |
|-------------------------------|----------------------|-----------------------|-----------------------------|----------------------|
| Rice husk activated carbon    | 0.40 ± 0.02          | 0.25 ± 0.06           | 0.59 ± 0.07                 | 0.78 ± 0.07          |
| Coconut shell activated carbon| 0.24 ± 0.01          | 0.11 ± 0.01           | 0.28 ± 0.04                 | 0.43 ± 0.03          |

In this study we investigated the adsorption characteristics, that is, the amount and rate of adsorption for four organic solvents, on rice husk activated carbon, and compared them with those of coconut shell activated carbon.

A comparison of the breakthrough curves for rice husk activated carbon and for coconut shell activated carbon showed that the former had less exhaustion time, that is, the time when the breakthrough concentration reached the inlet concentration, than the latter. This difference may have been partly due to the amount of activated carbon. Although the cell volume was the same, the weight of the activated carbon in the cells was different because the rice husk activated carbon had a smaller packing density; that is, 230 mg/cm³ for the rice husk activated carbon and 389 mg/cm³ for the coconut shell activated carbon. As a result, the adsorbed amount per unit of carbon volume of three of the four organic solvents used in this study was greater for the coconut shell activated carbon than for the rice husk activated carbon.

The adsorption affinity of organic solvents to activated carbon depends on their polarity; therefore we evaluated the effect of the polarity of organic solvents individually. First, the adsorbed amounts of ethyl acetate and toluene, which have low polarity, were 196.8 mg/g and 234.8 mg/g, respectively, in the rice husk activated carbon, whereas the adsorbed amounts in the coconut shell activated carbon were 262.8 mg/g for ethyl acetate and 364.6 mg/g for toluene. These results indicate that the adsorbed amounts of substances with low polarity were greater on the coconut shell activated carbon than on the rice husk activated carbon in both cases.

The adsorbed amount is also affected by specific surface area. The specific surface area of the rice husk activated carbon used in this study was about 960 m²/g [4], while that of other reported activated carbons made from rice husks varies from 500 to 2,700 m²/g, depending on activation [6–10]. On the other hand, the specific surface area of general activated carbons varies from 500 to more than 3,000 m²/g, depending on the material and activation [11–16]. Although the surface area of the coconut shell activated carbon used in this study was unknown, the experimental results showed that its unit adsorption capacity was about 1.6 times greater than that of the rice husk activated carbon for toluene and about 1.3 times greater for ethyl acetate. This suggests that the specific surface area of the rice husk activated carbon may have been smaller.
than that of the coconut shell activated carbon.

On the other hand, with acetone and methanol, which are highly polar compounds, the adsorbed amounts for the rice husk activated carbon were 81.3 mg/g for acetone and 8.0 mg/g for methanol, and those for the coconut shell activated carbon were 71.7 mg/g for acetone and 6.3 mg/g for methanol. These results showed that the rice husk activated carbon had a greater adsorption capacity for acetone than the coconut shell activated carbon ($P < 0.05$), and no significant difference was observed for methanol. These results, which were different from the results for toluene and ethyl acetate, could be due to the fact that the activated carbon had a weaker adsorption potential for highly polar substances and that the effect of surface area was less for low polar substances. The rice husk activated carbon was made from rice husk, and because rice is a high-silica plant, rice husk also contains silica [17]. Although the silica is removed during the manufacturing process of porous carbon materials, some of it remains in the product, and the high ash content may affect the amount of adsorption.

The slope of the breakthrough curve on the rice husk activated carbon was steeper than that on the coconut shell activated carbon ($P < 0.05$), suggesting that the adsorption rate of these substances is larger for rice husk activated carbon than for coconut shell activated carbon. The rice husk activated carbon that we examined in this study was made from rice husk with a high silica content, and a new process was introduced to remove the silica before activation. In the manufacturing process, pores are formed in the areas where the silica is removed, and previous research has reported that the pore size distribution is biased toward the larger side compared to existing activated carbons [4]. For example, the Barrett, Joyner, and Halenda (BJH) pore volume [18, 19], which is used to analyze the pore distribution of mesopores, was reported to be 0.5 cm$^3$/g for rice husk activated carbon, and 0.06 and 0.1 cm$^3$/g for a comparative activated carbon (coconut shell). Mesopores to macropores in rice husk activated carbon are also more developed than in a comparative activated carbon (coconut shell). A pore distribution map using the mercury injection method is also presented, revealing that the micropores in the rice husk activated carbon are smaller than those in the comparative activated carbons. The MP pore volume values used in the micropore analysis were reported to be 0.35 cm$^3$/g for rice husk activated carbon and 0.40, 0.47 cm$^3$/g for comparative activated carbons (coconut shell). The macro to mesoporous pore distribution facilitates fast intraparticle diffusion, which may be a factor in the high adsorption rate. Ammonia adsorption experiments were conducted using rice husk activated carbon in previous research [4], where it was reported that, at equal weight, the adsorption rate was faster than that of coconut shell activated carbon (different from that used in the present study) at the beginning of the experiment. In the present study, the rice husk activated carbon also showed a faster adsorption rate than the coconut shell activated carbon for four organic solvent vapors. These results suggest that faster adsorption rate is a characteristic of rice husk activated carbon, compared with coconut shell activated carbon. These results indicate that rice husk activated carbon has less adsorption capacity but a faster adsorption rate than the activated carbons typically used in respirator cartridges for organic vapors. Although its adsorption capacity is smaller, rice husk activated carbon can be applicable as an adsorbent for gas masks and working environment measurement because it has a faster adsorption rate and therefore removes harmful substances from the air more quickly.

**Conclusion**

The results of this study suggest that rice husk activated carbon has a lower unit adsorption capacity but a faster adsorption rate than coconut shell activated carbon for substances with low polarity, and a greater unit adsorption amount and a faster adsorption rate for substances with high polarity. Even though there are some limitations of the characteristics, rice husk activated carbon can become an alternative to coconut shell activated carbon in occupational and environmental measures because of its faster adsorption rate.

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**Conflict of Interest**

The authors declare that they have no conflict of interest.

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