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Ammonia Gas Adsorption by Carbonized Rice Husk

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Ammonia is a principal component of foul odors of agricultural and livestock wastes. This study investigated ammonia gas adsorption of rice husk carbonized in vacuum at different temperatures (300−800℃) for 3 h. In an enclosed bag, 1.00 g of the carbonized rice husk was exposed to ammonia gas at 100 ppm. Rice husk carbonized at 400℃ adsorbed ammonia the fastest. Its performance was much better than those of commercial deodorants. Pore characteristics and chemical characteristics of carbonized rice husk were examined to correlate them with the ammonia adsorption property. Remaining acidic functional groups were inferred to play a beneficial role in improving the ammonia adsorption.

Key Words : Rice husk, Carbonization, Ammonia, Adsorbent, Deodorant

1. INTRODUCTION

A huge quantity of rice husk (*ca.* 3 million tons) is produced every year as agricultural waste in Japan [1]. Rice husk incineration is now discouraged on farms. Only a fraction of rice husk is recycled in agricultural and livestock industries. It is therefore socially beneficial to convert rice husk into products that contribute to environmental improvement. Foul odor pollution produced by compost factories and livestock houses is becoming an important public concern even in suburban areas, which is related to a spread of people's residential districts. Compost factories and livestock houses are often adjacent to rice farms. An effective recycling methodology of rice husk could be created if we were able to convert rice husk into a deodorant material.

Ammonia is a principal component of foul odors produced from agricultural and livestock wastes. The characteristic nature of rice husk as biomass is a high content (*ca.* 20 mass%) of inorganic matter of which the major ingredient is SiO_2 [2]. In the present study, we carbonized rice husk in vacuum at different temperatures (300 − 800 ℃) to convert it into an ammonia adsorbent that is useful as a deodorant. The role of SiO_2 on several adsorption processes has been investigated [3]. We expect that SiO_2 in rice husk might interestingly enhance ammonia adsorption.

The effect of carbonizing temperature on ammonia adsorption was studied. The ammonia adsorption ability of the carbonized rice husk was compared to those of commercial deodorants. We analyzed the chemical and pore structures of carbonized rice husks, which suggested that acidic functional groups remaining at lower carbonizing temperature were useful to promote adsorption of basic ammonia gas.

2. MATERIALS AND METHODS

A rice husk sample was obtained by rice threshing at Akita Komachi rice grown in Ogata-mura (Akita Prefecture, Japan) in autumn of 2003. The inorganic content of the raw rice husk was determined from the residual-ash ratio after incineration at 815℃ for 1 h in atmospheric air. The ash composition was determined using a fluorescent X-ray analyzer (XRF-1700 ; Shimadzu Corp., Kyoto, Japan). A CHNO/S analyzer (2400 I ; PerkinElmer Inc., Boston, USA) was used to determine the hydrogen, carbon and nitrogen contents, as well as those of other elements. The raw sample was dried at 105℃ for 3 h prior to analyses. The analytical characteristics are tabulated in Tables 1 and 2. It is noteworthy that raw rice husk contains SiO_2 at *ca.* 20 mass%.

Table 1 Dry base composition of raw rice husk of Akita Komachi rice. Unit : mass%.

Ash	H	C	N	O* (by difference)
21.0	5.1	38.6	0.6	34.7

* : except for that in ash

Table 2 Composition of the ash from raw rice husk. Unit : mass%.

SiO_2	K_2O	P_2O_5	CaO	Detectable others
94.5	3.3	1.1	1.1	2.1

The rice husk was pyrolyzed in a stainless steel cylinder (SUS 304) whose respective external and bore diameters were 50 and 44 mm. The pyrolysis was carried out in vacuum (500 Pa) at 300 − 800℃ using an electrical furnace (KT-1053R ; Advantec Toyo Kaisha, Tokyo, Japan) and a vacuum pump system (PC610 ; Vacuubrand GmbH and Co. AG, Wertheim, Germany). The furnace temperature was increased linearly from room temperature to the desired pyrolysis temperature in 1 h ; it was then maintained at the desired temperature for 3 h. The furnace was then cooled naturally to room temperature. The vacuum level was maintained throughout pyrolysis. We call this rice husk, which has been pyrolyzed in vacuum, *carbonized rice husk*.

The rice husk was carbonized at 300－800℃, the raw rice husk and the commercial deodorant products were all dried for 3 h. It was verified beforehand that the above periods were sufficient to saturate the sample weights in drying. The samples were cooled at 22－24℃ and 30－40% RH, and then weighed 5 min later, after drying was completed. Then, the sample was enclosed quickly in a gas sampling bag made of polyvinyl fluoride film (Tedlar®; DuPont, USA) and residual air in the bag was degassed using a small pump for 5 min. Ammonia gas adjusted at the concentration of 100 vol ppm (dry air based, $<1\%$ RH@22－24℃) provided by Taiyo Nippon Sanso Corp., Tokyo, Japan, was injected 3 *l* to the degassed bag. The contact time started when the ammonia injection started. Kitagawa-type detecting tubes targeting ammonia gas (Komyo Rikakagaku Kogyo K.K., Tokyo, Japan) were used to measure the ammonia concentration in the bag. The gas of 100 m*l* in the bag was evacuated for every measurement of the ammonia concentration. The ammonia concentration was evaluated at 22－24℃ as a function of the contact time.

A gas-adsorption analyzer (Autosorb-1-MP; Quantachrome Instruments, FL, USA) was used to study the sample porosity, correlating it with the ammonia adsorption property. We obtained N_2 adsorption isotherms, providing the surface area based on the BET theory [4], and the total pore volume at a relative pressure of 0.995. The samples (*ca.* 0.02 g) were degassed at 200℃ for > 4 h prior to isotherm measurement. The BET surface area (S_{BET}) was calculated using the N_2 adsorbed volume at relative pressures (P/P_0) of 0.1－0.3. The liquid N_2 volume, referring to N_2 adsorbed volume at P/P_0 0.995, was determined to be the total pore volume (V_t). The volume of micropores (V_{micro}) was obtained following the t-method [5], giving the volume of mesopores and macropores ($V_{external}=V_t-V_{micro}$).

3. RESULTS

3.1 Ammonia Gas Adsorption Properties of Raw and Carbonized Rice Husk

The raw and carbonized rice husks were subjected to 100 ppm ammonia gas. We measured the ammonia concentration in the bag in which those rice husks were enclosed. Figure 1 shows the ammonia adsorption property of the raw rice husk and the rice husk carbonized at 300－800℃, of which weights were all adjusted to 1.00 g. The control indicates the ammonia concentration in the gas in which no sample was enclosed. Results showed that a slightly higher time-rate of the ammonia adsorption was observed on the rice husk that was carbonized at 300℃ than on the raw rice husk. With increasing carbonizing temperature, the time-rate of the ammonia adsorption increased at 300－400℃, whereas it decreased at 400－800℃. The rice husk carbonized at 600－800℃ required a much longer time to reduce the ammonia concentration (<10 ppm) than the raw rice husk did.

The carbonizing temperature had a large influence on the ammonia adsorption of rice husks. The fastest adsorption performance appeared on the rice husk carbonized at 400℃, which reduced the ammonia concentration <5 ppm in 30 min. High carbonizing temperature (>600℃) was found to be unnecessary to enhance ammonia adsorption.

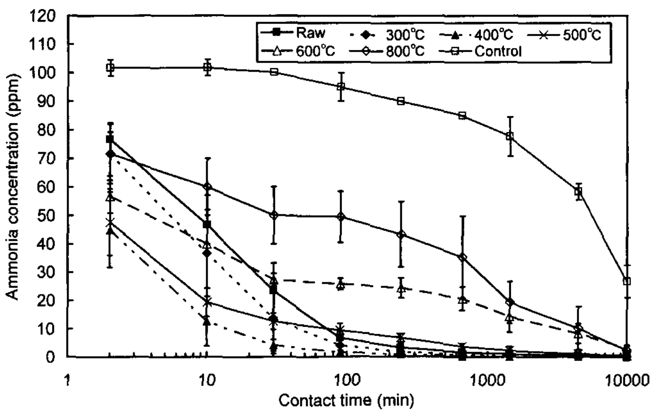

Figure 1 Ammonia adsorption of raw rice husk and the rice husk carbonized at 300－800℃ as a function of contact time. The sample weight was 1.00 g.

Table 3 Descriptions of commercial deodorants used for comparison with carbonized rice husks.

Sample ID	Product	Primary ingredient	Manufacturer
Activated carbon	Refrigerator deodorant sand	Coconut shell activated carbon	Kobayashi Pharmaceutical Co., Ltd.
Silica gel	Deodorant sand	Silica gel (SiO_2)	Unicharm Corp., Japan
Wood chip pellet	Antibacterial (deodorant) chips	Raw woods in Germany	Kao Corp., Japan

3.2 Comparison of Ammonia Gas Adsorption of Carbonized Rice Husk with Commercial Deodorants

Different types of commercial deodorants that are useful for adsorption of ammonia gas were evaluated similarly; they were compared with the rice husk carbonized at 400℃, which displayed the best performance in the above test. Activated carbon, silica gel, and wood chip pellets, of which details are described in Table 3, were employed as reference commercial deodorants.

Figure 2 shows the ammonia gas adsorption property of commercial deodorants and the rice husk carbonized at 400℃.

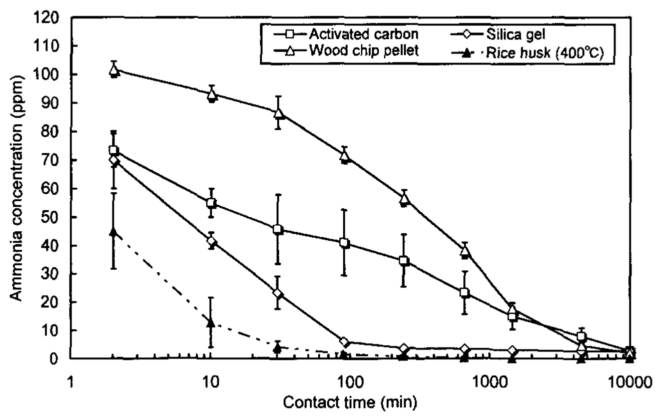

Figure 2 Ammonia adsorption of different types of commercial deodorants and rice husk carbonized at 400℃. Sample weights were adjusted to 1.00 g. Results of the rice husk shown here are similar to that shown in Figure 1.

Table 4 Compositional changes and yields of the carbonized rice husks. Oxygen content is calculated : O = 100 − (C + H + N + ash). The unit of the composition and the yield is mass%.

Carbonizing temperature (℃)	H	C	N	O	Ash	Yield
Raw	5.1	38.6	0.6	34.7	21.0	100.0
300	3.5	41.2	0.4	17.7	37.2	56.5
400	2.3	43.0	0.4	9.2	46.9	44.8
500	2.0	41.2	0.4	4.2	50.4	41.7
600	1.1	42.2	0.3	1.6	54.8	38.3
800	0.5	42.0	0.5	2.6	54.4	38.6

Table 5 Pore characteristics of the raw and carbonized rice husks.

Carbonizing temperature (℃)	S_{BET} (m^2/g)	V_t (ml/g)	V_{micro} (ml/g)	$V_{external}$ (ml/g)
Raw	1.7	0.012	0	0.012
300	8.7	0.029	0	0.029
400	52.2	0.083	0	0.083
500	64.0	0.095	0	0.095
600	170.0	0.165	0.038	0.127
800	59.9	0.101	0	0.101

Results showed that the carbonized rice husk adsorbed ammonia gas in a much shorter time than commercial deodorants. The carbonized rice husk required 30 min to reduce the ammonia concentration < 5 ppm, whereas the silica gel, which displayed the fastest ammonia adsorption of all the commercial deodorants, required *ca.* 150 min. That result demonstrates that the ammonia adsorption performance of the carbonized rice husk was superior to several types of commercial products.

3.3 Pore and Chemical Characteristics of Carbonized Rice Husk

The ammonia gas adsorption of the carbonized rice husk is inferred to be correlated with its pore and chemical characteristics. Changes in the composition and yield of the rice husk carbonized in vacuum at 300 − 800℃ for 3 h are shown in Table 4 as a function of the carbonizing temperature. Results showed that the yield of the carbonization process decreased up to 600℃ and remained at a similar level of 38 mass% at higher temperatures. The carbon content of the carbonized rice husk changed only slightly. The hydrogen and oxygen contents of the rice husk carbonized at 300 − 500℃, which displayed faster ammonia adsorption, were higher than those of rice husk that had been carbonized at 600 − 800℃. That fact implies that the remaining hydrogen and oxygen might be related to enhancement of the ammonia adsorption. It is also noteworthy that about half of the weight of the rice husk carbonized at > 300℃ is attributable to ash (primarily SiO_2).

Pore structures of the carbonized rice husk were analyzed. All isotherms except for that of the raw rice husk were found to belong to Type II, as categorized by the BDDT classification [5]. The relative surface area (S_{BET}) and the pore volume information (V_t, V_{micro} and $V_{external}$) were obtained. Table 5 shows pore characteristics of raw and carbonized rice husks. Between 300 − 600℃, S_{BET} and V_t increased with the carbonizing temperature. At higher temperatures, S_{BET} and V_t decreased with the carbonizing temperature. The most porous structure was observed on the rice husk carbonized at 600℃. Micropores of which pore diameter is < 2 nm were produced in the rice husk that had been carbonized at 600℃.

Those results described above indicate that the fastest ammonia adsorption was apparent for the rice husk carbonized at 400℃. However, the most porous structure appeared on the rice husk carbonized at 600℃. Porosity probably does not play a predominant role in determining their ammonia adsorption performance. However, only a decrease in the time-rate of the ammonia adsorption with the carbonizing temperature at 600 − 800℃ might be attributed to the degeneration of pores.

4. DISCUSSION

The carbonizing temperature strongly influenced the ammonia adsorption of rice husks. Their pore structure was revealed to have a tenuous relation to their ammonia adsorption. Carbonizing temperatures < 400 ℃ can enhance ammonia adsorption capabilities, whereas temperatures > 400℃ do not. As described previously, the rice husk carbonized at 300 − 500℃, which showed the fastest adsorption performance, allowed higher contents of hydrogen and oxygen than other carbonized rice husks. Functional groups such as hydroxyl (−OH), carboxyl (−COOH), and carbonyl (>C=O) groups were likely to be rich in the rice husk carbonized at 300 − 500℃. It was pointed out in two other studies [6, 7] that acidic functional groups produced by carbonization at 400℃ can promote ammonia gas adsorption in other species of biomass (*e.g.*, Japanese cedar and Japanese cypress). Acidic carboxyl groups can promote adsorption of ammonia molecules through a neutralization process illustrated in Eq. 1.

$$-COOH + NH_3 \dashrightarrow -COONH_4 \quad (1)$$

On the other hand, we must recognize that the above polar functional groups can adsorb ambient moisture. Equation 2 shows that ammonia molecules can be dissolved into moisture.

$$H_2O + NH_3 \dashrightarrow OH^- + NH_4^+ \quad (2)$$

The ammonia adsorption test was implemented in dry air (< 1% RH). However, residual moisture might be involved in this process. An evaluation of hygroscopic properties of the sample rice husk provides helpful information connected to a mechanism of the ammonia adsorption of rice husk. Raw and carbonized rice husk samples (1.00 g) were dispersed on glass petri dishes (60 mm diameter). They were then placed in a chamber (50 × 50 × 50 cm^3) in which the temperature and the humidity were controlled respectively as 25 − 27℃ and 78 − 82 % RH. The weight changes of the samples resulting from exposure to humid air were evaluated (see Figure 3). The control indicates the results for no sample on a glass petri dish. Exceptionally, the raw rice husk adsorbed much moisture. The largest amount of moisture uptake in the carbonized rice husk appeared for the sample that had been carbonized at 400℃. Less moisture uptake was apparent for that carbonized at 600 − 800℃ than for samples carbonized at 300 − 500℃. The weakest moisture uptake appeared at 600℃, which was commonly observed in other carbonized biomass species [8]. A stronger moisture uptake of rice husk carbonized at 300 − 500℃ seems to be consistent with their faster ammonia adsorption. However, the raw rice, showing the greatest moisture uptake, was shown to adsorb less ammonia than the rice husk carbonized at 400℃, as depicted in Figure 1. The raw rice husk and the rice husk carbonized at 800℃ should have adsorbed more ammonia gas if moisture uptake were a dominant mechanism of ammonia adsorption. The lesser moisture uptake ability of the raw rice husk and the rice husk carbonized at 300℃ seems to be attributable to the loss of wood constitution, particularly the loss of hydrogen and oxygen elements. Formation of polar functional groups is likely to regain the moisture uptake ability, which is relevant to the change in hygroscopic nature of rice husk carbonized at 300－500℃.

It is described in one study [9] that acidic carboxyl groups, rather than basic carbonyl groups, are readily produced at lower temperatures during biomass pyrolysis (carbonization). Table 4 shows that the hydrogen content of the rice husk carbonized at 600－800℃ decreased to lower levels (*ca.* 1 mass%), implying that basic carbonyl groups were richer than acidic carboxyl groups in this temperature range.

Consequently, the fastest ammonia adsorption of the rice husk carbonized at 400℃ was deemed to result from formation of acidic carboxyl groups, in which Eq. 1 should have proceeded predominantly. The higher carbonizing temperature (>400℃) reduced carboxyl groups and might produce carbonyl or other functional groups instead. Hence, the ammonia adsorption capability of carbonized rice husk diminished with increasing carbonizing temperature. The ammonia adsorption of the raw rice husk is inferred to be the result of a strong hygroscopic nature derived from intrinsic celluloses. In this adsorption, Eq. 2 probably describes the primary process. The ammonia desorption process of the raw and the carbonized rice husks will be studied in depth in future studies to verify the above inference.

The role of SiO_2 in the ammonia adsorption by carbonized rice husk should also be discussed. Compositional analyses shown in Table 4 indicate that the SiO_2 (ash) content increased with increasing carbonizing temperature. It was further demonstrated that the ammonia adsorption ability was not enhanced simply with the carbonizing temperature. Therefore, we conclude that the contribution of SiO_2 in rice husk to its ammonia adsorption was minor.

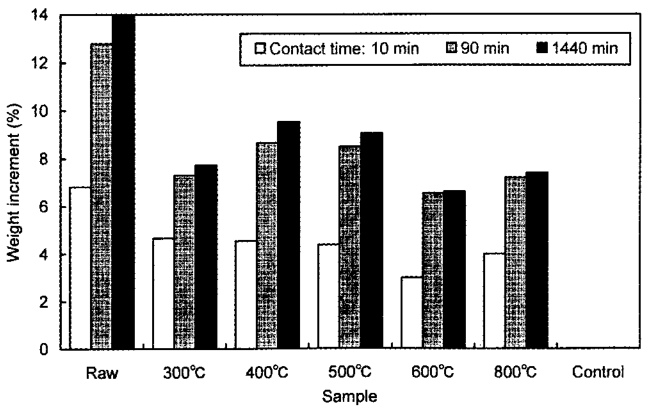

Figure 3 Weight increment of the raw rice husk and rice husk carbonized at 300－800℃ in humid air (78－82% RH@25－27℃) as a function of contact time. The sample weight prior to the test (dried state) was 1.00 g.

5. CONCLUSIONS

This study evaluated ammonia gas adsorption capabilities of rice husk carbonized in vacuum at different temperatures (300－800℃) for 3 h. The adsorption performance was strongly dependent on the carbonizing temperature. Rice husk carbonized at 400℃ displayed the fastest ammonia adsorption, which reduced the ammonia concentration in the bag of 3.0 *l* from 100 to 5 ppm in 30 min. This performance was far superior to those of several commercial deodorants. The ammonia adsorption of the carbonized rice husk was only slightly relevant to its pore structure. Results suggest that acidic functional groups played an important role in ammonia adsorption.

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