Deodorizing Ability of a Diatomaceous Material as an Environmentally-Friendly Inner-Wallboard

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健康建材として用いられているケイ質頁岩材料の脱臭能の評価

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Deodorizing ability of a diatomaceous material mined from Wakkanai district in Hokkaido Pref. was examined in detail. This material is widely distributed in the market as a material of environmentally-friendly inner-wallboard. Alternative introductions of a model odor {NH_3, CH_3CHO, or $(CH_3)_2S$} mixed-N_2 gas flow and a pure N_2 gas flow into the diatomaceous material showed reversible adsorption and desorption of the odor components at 25°C, reconfirming regeneration of deodorizing ability for the diatomaceous-wallboard by ventilation of rooms with these wallboards. The adsorbed quantities of the odors onto the diatomaceous material during one hour readily cleared the odor level 3: 2.3 ppm for NH_3, 0.14 ppm for CH_3CHO, and 0.044 ppm for $(CH_3)_2S$, respectively. [Received October 15, 2001; Accepted February 15, 2002]

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1. Introduction

As is well-known, the increases in the amount of the VOCs such as formaldehyde, toluene, and xylene, etc., being used as plasticizers and adhesives in floorboards, inner-wallboards, and wall-cloths, have been causing serious symptoms of the sickhouse(the sickbuilding) syndrome. One of the effective solutions against this problem should be to use natural material-originating boards or cloths.

Recently, an algae-originating mineral, a diatomite has recieved much attention as a material of environmentally-friendly inner-wallboards.[1] In Wakkanai district in Hokkaido Pref., a diatomaceous material (designated DM) is mined and is supplied to the market as an inner-wallboard having the prominent self-humidity controlling function compared with any other diatomite and material,[2),3)] keeping comfortable humidity between 50-70% in rooms. In order to keep good conditions of human health, a simultaneous controlling of both the humidity and the indoor concentration of various chemicals and odors is desirable. However, deodorizing ability of DM has not been evaluated practically concerning both durability and contributions to a decrease in the odor level in rooms. In this paper, adsorption and desorption properties of model odor gases on DM were investigated in two different systems: a flow and a batch ones, paying attention to the practical deodorizing ability.

2. Experimental

2.1 Samples

The diatomaceous material (DM) used in this study was supplied by Suzuki Sangyo Co.[4] Its chemical composition is summarized in Table 1. The DM was mineralized more than any other diatomite and was composed of several minerals such as quartz, a feldspar, and so on.[5] The BET specific surface area and the average pore radius were 127.5 m^2/g and 3.73 nm, respectively, and most of the pores were ranging from 1-10 nm.[2] For the adsorption experiments, DM was sieved to 14-20 meshes. Two commercial deodorants: an active carbon (AC) and a bentonite-based material (BN) were employed as references in order to evaluate the deodorizing properties of DM, and their surface areas were 1000 and 61 m^2/g, respectively.

Table 1. Chemical Composition for Cations of a Diatomaceous Material in Wakkanai District

Component	mol %
Si	80
Al	11
Na	1.3
K	3
Fe	3
Mg	0.9
Ca	0.4
Ti	0.4

CH_3CHO, NH_3, and $(CH_3)_2S$ were chosen as the model chemicals of odors, which were generated by tobaccos, pets, and garbage, and so on in houses. CH_3CHO and $(CH_3)_2S$ were reagents from Wako Pure Chem. Ind. Co., Ltd., and Tokyo Kasei Kogyo Co., Ltd., respectively. Their purities were higher than 88% for CH_3CHO, and higher than 99.0% for $(CH_3)_2S$. NH_3 was supplied from a NH_3 (25%)-aqueous solution from Wako Pure Chem. Ind. Co., Ltd.

2.2 Apparatus

Adsorption behavior was examined with two experimental systems; a batch system and a flow system. Each system is schematically shown in Figs. 1 and 2, respectively. For the batch system in Fig. 1, after a 100 ppm (odor)-N_2 stream was introduced into a glass flask of 100 ml (6) for 10 min, the gas flow was cut with two needle valves (2). About 1 g of adsorbents were put into the flask as soon as it was cut. The concentrations of the odors in the closed flask were analyzed and the concentration decay curves due to the adsorption of the odors onto the adsorbents were obtained. The decreases in total pressure in the flask due to adsorption of the odor were negligibly small compared with the initial pressure of 1 atm.

Transient response method was employed for the flow system. This method is used to elucidate the catalytic reaction mechanisms by analyzing unsteady states induced by perturbing a given reaction condition, e.g. gas composition, pressure, temperature, etc.[6] Figure 2 shows the experimental setup. 1 g of the adsorbent was packed in a Pyrex glass tube of 6 mm in i.d. (8) and an odor-N_2 stream and a N_2 stream were introduced into the glass tube alternatively. Switching of the gases were done several times with a four-way valve (5), where difference in the pressures between the two gas streams was kept nearly zero by adjusting two needle valves (9) and a manometer (4). The adsorbed amount of the odor during each procedure was estimated from the integration of the decay curve to a steady state of a given odor concentration; and the desorbed amount was estimated from the curve to zero in a N_2 stream.[7] Each adsorption and desorption curve obtained was re-drawn by subtracting blank values from the observed values, because the observed ones had both adsorption on the inside wall of the glass tube for the gas flow and deviation from ideal step functions between N_2 and the odor-mixed N_2 gas flows, as well as the adsorption of the odors on the deodorants.

The odor gases were supplied from a N_2 gas flowing through the liquids in a buffer flask. Gas analysis was done with two gas chromatographs equipped with a flame ionization detector for CH_3CHO and $(CH_3)_2S$, and a thermal conductivity detector for NH_3. The column packings used were Porapak *Q* for CH_3CHO and $(CH_3)_2S$, and Porapak N for NH_3, respectively, and each column bath temperature was 150°C for CH_3CHO, 180°C for $(CH_3)_2S$, or 100°C for NH_3.

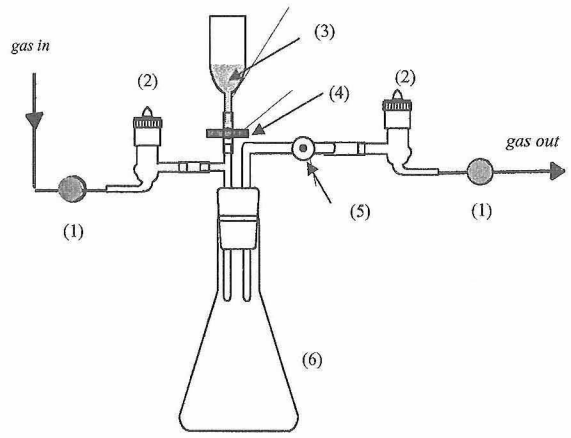

Fig. 1. Deodorizing experimental setup of the batch system. (1) Stop valve, (2) needle valve, (3) sample granule, (4) pinch cock, (5) sampling hole, (6) glass flask of 100 ml in volume.

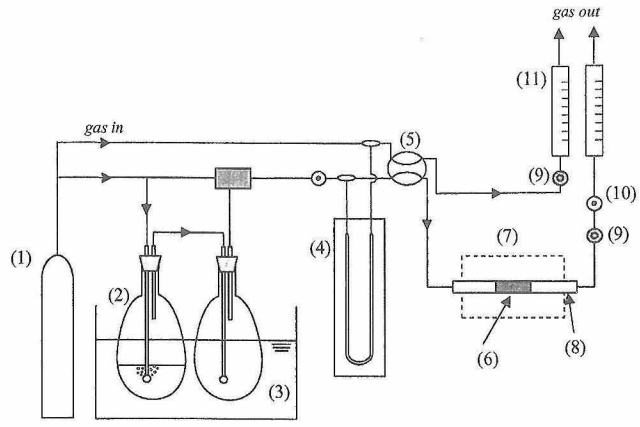

Fig. 2. Deodorizing experimental setup of the flow system (1) nitrogen gas cylinder, (2) vaporizing glass flask, (3) water bath, (4) mercury manometer, (5) four-way valve, (6) sample granule, (7) electric furnace, (8) Pyrex glass tube, (9) needle valve, (10) sampling hole, (11) soap film meter.

3. Results and discussion

3.1 Adsorption behavior of NH_3, CH_3CHO, and $(CH_3)_2S$ on the diatomaceous material with a batch system

Figures 3(a), (b), and (c) show the gaseous concentration decay curves of NH_3, CH_3CHO, and $(CH_3)_2S$ onto DM, and two commercial deodorants; BN and AC at 25°C, being caused by progress of adsorption. The coordinates designates the concentration of the gases as a function of time, where the values are obtained by subtracting the blank from the observed values. One can see that the three gases adsorbed on all the materials at the elapsed time. Slope of each decay curve was larger at the first stage of the adsorption for the first 5 min than that in the last stage from 20 to 100 min. The steeper slopes of the decay curves at given times mean that the adsorption rates at the times are larger. Therefore, the adsorption rates at the initial stages are larger than those at the later stages for all the experimental curves. The adsorption rate generally depends on the concentration of gas and the quantity of vacant sites for the adsorption, i.e., $r=k\cdot p\cdot\theta_V$, where r is adsorption rate (ppm/min·g), k is adsorption constant (1/min·g), p is gaseous concentration of odor (ppm), and θ_V is the ratio of the amounts of the vacant sites to those of the total active sites for the odor adsorption (−). The decay of the adsorption rates, therefore, resulted from the reduction of θ_V, that is to say, the odor molecules dominated the surface of the deodorants at elapsed time.

For the evaluation of the adsorption rates for DM, AC, and BN, the slopes of the decay curves at the middle point of each stage: at 2.5 min for the first stage (designate $r_{2.5}$) and at 60 min for the last stage (designate r_{60}) are chosen, respectively. The values obtained were compared in Table 2. The $r_{2.5}$'s are ten to thirty times the r_{60}'s for all the deodorants, confirming the much larger adsorption rates at 2.5 min. DM offers a comparable adsorption rate with AC and BN, and therefore, DM has been found to be a promising deodorant on the market as well as self-humidity controlling material.

3.2 Durability of deodorizing ability of the diatomaceous material with a flow system

Deodorizing durability of DM has been examined with repeatedly alternative introductions of the odor-mixed N_2 and pure N_2 gases. Figure 4 shows the adsorption and desorption curves of NH_3 onto DM at 25°C. The

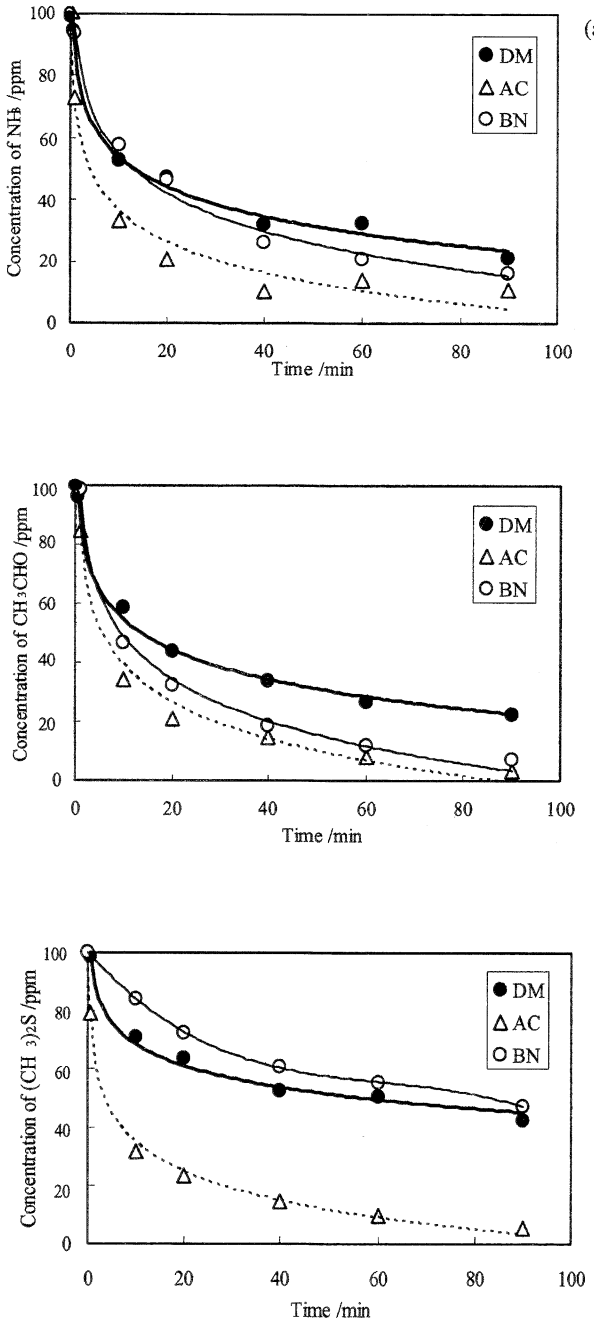

Fig. 3. Adsorption behavior of (a) NH_3, (b) CH_3CHO, and (c) $(CH_3)_2S$ onto the three samples at 25°C in a batch system.

monotonous increase and decrease in the curves indicate that its adsorption and desorption occur repeatedly. Regenerating adsorption in NH_3-mixed N_2 and desorption processes in N_2 gases suggested that the surface sites for adsorption was regenerated during the N_2 flowing process. From the result, deodorizing ability of DM is considered to be sustainable with an appropriate ventilation procedure in rooms.

The adsorbed and desorbed amounts during each run for DM, AC, and BN were estimated from graphical integrations of the shaded areas of each run in Fig. 4 and the results are shown in Fig. 5. All the values are designated as the ratios of the adsorbed or desorbed amount during each run to the adsorbed amount during the first run, where the initially adsorbed amounts are estimated to be 5.0, 8.9, and 4.9×

Table 2. Comparison of Adsorption Rates at (a) 2.5 min and (b) 60 min

(a)

	DM	BN	AC
NH_3	**4.8 (±0.5)**	**6.3 (±0.5)**	**5.3 (±0.5)**
CH_3CHO	**6.6 (±0.6)**	**8.9 (±0.6)**	**8.6 (±0.6)**
$(CH_3)_2S$	**3.5 (±0.3)**	**1.6 (±0.2)**	**5.8 (±0.7)**

(ppm/g·min)

(b)

	DM	BN	AC
NH_3	**0.22 (±0.02)**	**0.28 (±0.03)**	**0.21(±0.03)**
CH_3CHO	**0.25 (±0.02)**	**0.34 (±0.03)**	**0.27 (±0.03)**
$(CH_3)_2S$	**0.17 (±0.02)**	**0.16 (±0.02)**	**0.20 (±0.02)**

(ppm/g·min)

10^{-7} mol-NH_3/g-sample, respectively. For all the samples, both the second and the third adsorption are comparable, and less than the initial adsorption. (30–35% for DM, 10–20% for AC, and 20–30% for BN, respectively) The highest adsorption of the first run suggests that this run involves both irreversible and reversible adsorptions, while the second and third adsorption processes are associated with only reversible adsorption, because the reversibly adsorbed odor could be reasonably desorbed during the cleaning of the surface with the N_2 gas stream as opposed to the irreversible one which could be tightly held on the surface.

Furthermore, the first and the second desorptions on DM and BN are almost half of the second and third adsorption processes. For AC on the contrary, all the adsorbed and desorbed amounts are comparable. Our interest is focused on this difference of adsorption-desorption behavior between DM, BN and AC. Crystal clays having layered structure such as bentonite are known to be swollen by incorporation of water or other solutions into its interlayers.[8)-10)] BN used in this study has exchangeable cations: Na^+ of 8.1 mol% and Mg^{2+} of 3.8 mol%, and its interlayer distance is 0.88 nm.[11)] Therefore, it has been considered that NH_3 accompanied with water entered into the bulk of BN, which is bentonite-based material, and swelling of BN occurs during adsorption of NH_3. DM also has some kinds of clay materials,[4)] and one of them has a layered structure whose layered distance is about 1.0 nm[11)] although the intensity of the XRD peak is not high. Therefore the similar structural change could happen to DM. As shown in Fig. 4, it takes about 12–15 min for each adsorption process to complete while 7–8 min at most for the desorption processes. This result can be explained by an idea that a part of NH_3 together with water enters into the bulk of DM during the adsorption processes as mentioned above, and these NH_3 molecules do not desorb out of DM in the flow of N_2.

3.3 Evaluation of the deodorizing ability of a diatomaceous material

Based on the results in the batch system, deodorizing ability of DM has been evaluated in terms of the odor level, regulated by the Ministry of Environment of Japan. The ad-

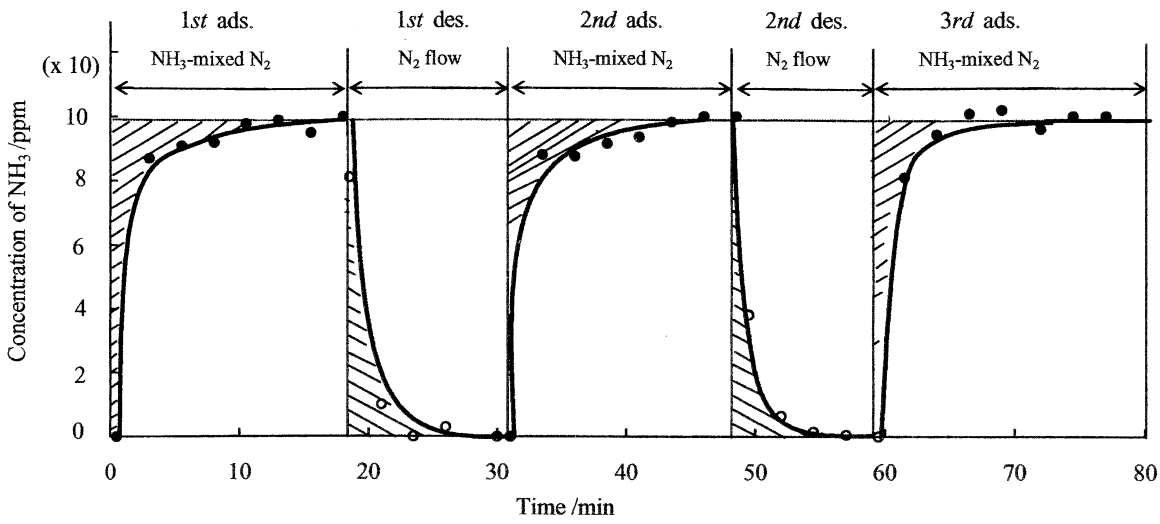

Fig. 4. Adsorption and desorption behavior of NH_3 on DM at 25°C in a flow system.

Table 3. Evaluation of Deodorizing Ability of the DM Wall-Board

odor	Concentration of odor removed by DM after 60 min x [ppm]→0 *1	Concentration of *the odor level 3*2* [ppm]
NH_3	3.8	2.3
CH_3CHO	3.6	0.14
$(CH_3)_2S$	2.6	0.044

*1 20% of the wall is covered with DM wall-board; 6.9 m^2 in the room of 31.1 m^3 in space, and 1.14 kg-DM is available for deodorization, i.e., the 1 mm-layer of the surface of the DM wall-board

*2 Easily sensible level: regulated by the Ministry of Environment of Japan

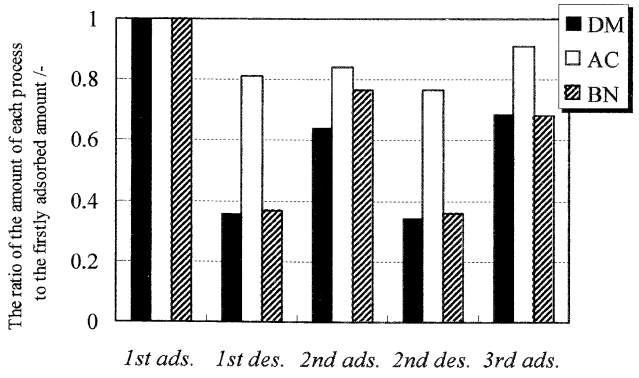

Fig. 5. Ratios of the amount of each adsorption and desorption process to the initially adsorbed amount of NH_3 at 25°C for the three samples.

sorbed amounts of NH_3, CH_3CHO, and $(CH_3)_2S$ during an hour has been estimated inside a room with 31.1 m^3 (3.6×3.6×2.4 m) in space which equals to that of 8 mat-room. Two assumptions were suggested for the estimation: 20% of the wall of the room (about 6.9 m^2) was covered with the DM board and its 1 mm thick was available for adsorption of the odors, where the weight of DM available for adsorption of the odors was estimated to be 1.14 kg/m^2 of the wall. The results in Table 3 mean that 3.8, 3.6, or 2.6 ppm of NH_3, CH_3CHO, and $(CH_3)_2S$ inside the room of 31.1 m^3 in space, respectively were adsorbed during an hour by the DM board. These values were larger than those of *the odor level 3*,[12] 2.3, 0.14, and 0.044 ppm, respectively (easily sensible level), leading to an idea that *the odor level 3* can be cleared by the DM board for these three odors.

Although our estimation is limited to the local adsorption behavior in rooms, the integration of the results is considered to reflect the deodorizing properties in the space. Furthermore, the estimation is done only about the adsorption behavior of the odors in a dry condition of relative humidity less than 10%. Therefore two important points to be clarified are left: desorption behavior of the odors and the effect of the co-existing gases, in especial steam, on the adsorption and desorption behavior. Experimental results concerning these points will be reported in the next paper. Another investigation is also in progress in order to add more sustainable deodorizing ability to DM, modifying it chemically and physically with another component such as TiO_2.

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