

Comparison of the Biological H₂S Removal Characteristics among Four Inorganic Packing Materials

MITSUYO HIRAI, MANABU KAMAMOTO, MOHAMAD YANI, AND MAKOTO SHODA*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226–8503, Japan

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Four inorganic packing materials were evaluated in terms of their availability as packing materials of a packed tower deodorization apparatus (biofilter) from the viewpoints of biological H₂S removal characteristics and some physical properties. Among porous ceramics (A), calcinated cristobalite (B), calcinated and formed obsidian (C), granulated and calcinated soil (D), the superiority of these packing materials determined based on the values of nonbiological removal per unit weight or unit volume of packing material, complete removal capacity of H₂S per unit weight of packing material per day or unit volume of packing material per day and pressure drop of the packed bed was in the order of A ≈ C > D ≈ B, which is correlated with the maximum water content, porosity, and mean pore diameter.

[Key words: biofilter, hydrogen sulfide, removal capacity, inorganic packing materials]

The applications of biological deodorizing methods have been increasing (1–4) because of their cost effectiveness and simple maintenance (2, 5) compared to chemical and physical methods. Biological deodorizations are divided into two types of system, gas-solid and gas-liquid systems (6). Among the gas-solid systems, a packed tower deodorization system is efficient mainly because this can be constructed in a small construction area and can function sufficiently in urban areas. To reduce the scale of the apparatus, the selection of packing materials is an important factor and many different types of packing materials suited for microbial growth have been actively researched. Some requirements for a good packing material are as follows: (i) high water-holding capacity, (ii) high porosity and large specific surface area, (iii) less compacting nature, (iv) low-pressure drop over a wide range of water content, (v) small change in form in long periods of use, (vi) lightness, (vii) low cost, (viii) appropriate adsorbing ability for malodorous gases and (ix) large buffering capacity for acidic end products. Requirements (iii), (iv), (v), (vi) and (vii) are mainly related to the construction and maintenance of the biological deodorization apparatus, and (i) and (ii) are related to its biological activities. The acidity or basicity of gases may be one of the factors for selecting packing materials. As organic packing materials, soil, compost and peat were shown as good packing materials (7–14) that meet requirements (i), (ii), (vii), (viii) and (ix). Inorganic packing materials, such as perlite (15), porous ceramics (16), activated carbon fiber (17,18) and porous lava (19), are used, because they meet requirements (iii), (iv) and (v). Because comparative study of different packing materials has been rarely conducted under the same condition (20), the evaluation of many packing materials is difficult. In this study, biological H₂S removal characteristics of four inorganic packing materials were evaluated under the same experimental conditions of packing volume, flow conditions and inoculation source. Additionally, the H₂S removal characteristics were discussed in terms of physicochemical properties and microbial

distribution on the packing materials.

MATERIALS AND METHODS

Flow system A gas flow system is shown in Fig. 1. Biofilter columns are made of glass and have a 50 mm inner diameter and 500 mm height. H₂S gas from a gas cylinder was diluted with air from a compressor, then supplied to the biofilter downward after its flow was regulated with a flowmeter to the appropriate value.

Packing materials The chemical components of the inorganic packing materials used are shown in Table 1. True density (g·cm⁻³), porosity (%), bulk density (g·cm⁻³), mean pore diameter (μm), pore distribution, pH, and maximum water content (%) were measured as follows.

True density (ρ_2): distilled water was placed into a 100-ml Erlenmeyer flask. A mark was made at the water level inside and the system was weighed [y_1 g]. Fifty ml of distilled water and x g of packing material dried at 100°C overnight were placed in the marked flask, then stirred with a magnetic stirrer and suctioned with an aspi-

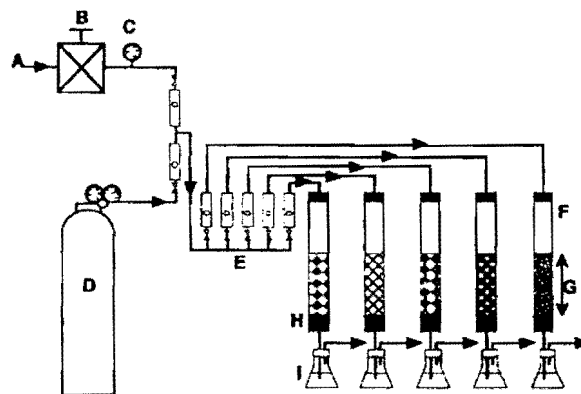


FIG. 1. Schematic of laboratory-scale experimental apparatus. A, Air; B, pressure regulator; C, pressure gauge; D, gas cylinder (H₂S + N₂); E, flow meter; F, glass column (50 mmφ × 500 mmH, packed height 180 mmH); G, packing material; H, saran net; I, drain water.

* Corresponding author. e-mail: mshoda@res.titech.ac.jp
phone: +81-(0)45-924-5274 fax: +81-(0)45-924-5276

TABLE 1. Chemical components of the packing materials used (wt.%)

Packing material	Chemical components							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
A: Porous ceramics	85.9	6.3	0.1	0.2	1.4	0.3	0.4	1.6
B: Calcinated cristobalite	80.3	9.8	3.1	0.4	0.2	2.9	0.3	1.5
C: Calcinated and formed obsidian	78.2	13.1	0.7	0.1	0.6	0.1	2.1	4.5
D: Granulated and calcinated soil	55.7	22.0	13.6	2.0	1.9	2.0	0.1	3.3

rator for 1 h. Distilled water was added at the marked level and the system was weighed (y_2 g), and ρ_a was calculated as follows.

$$\rho_a = x / (x - (y_2 - y_1)) \quad (1)$$

Porosity (ϵ): each packing material and distilled water were placed in a 100-ml volumetric cylinder, and their total volume (V_1 ml) was measured. Then, the volume of the packing material (V_a) was calculated using the following equation.

$$V_a = V_1 - (y_2 - y_1) - 50 \quad (2)$$

Here, [weight of added water] = [volume of added water] = [pore volume of the packing material].

Porosity was determined by the following equation.

$$\epsilon = (y_2 - y_1) / [(y_2 - y_1) + V_a] \times 100 \quad (3)$$

As packing materials C and D floated on the water surface, their true density and porosity were measured by the following method. Fifty ml of distilled water and the packing material (x_1 g) were placed into a 100-ml of Erlenmeyer flask and suctioned using an aspirator. The weighed packing material (x_2 g) taken out from the flask and 20 ml of distilled water were placed into a graduated cylinder, and their total volume (V_1 ml) was measured. Apparent porosity was obtained using the following equation.

$$\text{Apparent volume} = V_1 - 20$$

True density and porosity were calculated from the apparent volume.

$$\rho_a = x_1 / \{(\text{apparent volume}) - (x_1 - x_2)\} \quad (4)$$

$$\epsilon = \{(x_1 - x_2) / (\text{apparent volume})\} \times 100 \quad (5)$$

Bulk density (ρ_b): bulk density was calculated as follows.

$$\rho_b = \rho_a (1 - \epsilon) \quad (6)$$

Mean pore diameter (μm) and pore distribution (μm)

TABLE 2. Packing conditions

Packing material	Packed height (cm)	Packed weight (g-dry)	
		Experiment on nonbiological removal of H ₂ S	Experiment on biological removal of H ₂ S
A	18	86.0	53.1
B	18	233	194
C	18	39.1	38.6
D	18	139	188

were measured using the mercury pressure porosimeter method (porosimeter Type 220, Carlo Erba Strumentazione, Co. Ltd., Italy). The pH, maximum water content and water retentivity were measured by the same methods described in a previous paper (20).

Nonbiological H₂S removal on packing material A dry packing material (y_1 g) was soaked in water overnight, then packed in a glass column at 18 cm height under the same conditions as those in the flow experiment shown in Fig. 1. Packing material C with low density was floated on the water surface and suctioned using an aspirator to remove air inside of it. Then, it was placed back to atmospheric pressure to allow water absorption into the micropore. After no water was dripping from the bottom of the column with maximum water content, 100 ppm H₂S at about 60% relative humidity of atmosphere was made to flow in the downstream direction at 0.7 l/min (SV=119 h⁻¹). The load per unit volume of packing material to each column was set at the same value of 408 g-S·m⁻³ packing material·d⁻¹. Loads per unit weight of packing material are different, because of their different packing densities. Detailed packing conditions are shown in Table 2.

Biological H₂S removal To seed the microorganisms, each packing material was soaked in the sludge taken from a reservoir tank for UF film separation of a nondilution and high-load night soil treatment plant. Packing materials inoculated with sludge were packed in the column at 18 cm height and H₂S was supplied at 22°C. The load of the gas on each column increased gradually by changing the inlet concentration and/or space velocity, and the pH of each column was neutralized by NaHCO₃ or HCl (see legend in Fig. 4).

Microbial count Cell numbers were measured at the start and at the end of the experiment. About 10 g (wet weight) of each packing material was sampled and homogenized in 90 ml of sterilized water at 10,000 rpm for 10 min (Homogenizer EX-3, Nihon Seiki Ltd., Tokyo). Serially diluted suspension was streaked onto the following solid media: nutrient agar containing yeast

TABLE 3. Media used for microbial count in H₂S removal (g·l⁻¹)

NYA	CDA		DMSOA		MWG		TSA		
Meat extract	3	Glucose	30	K ₂ HPO ₄	1.55	KH ₂ PO ₄	8	KH ₂ PO ₄	2
Polypepton	15	K ₂ HPO ₄	1	NaH ₂ PO ₄	0.85	NH ₄ Cl	0.1	K ₂ HPO ₄	2
Yeast extract	3	MgSO ₄ ·7H ₂ O	0.5	NH ₄ Cl	2	CaCl ₂ ·2H ₂ O	0.5	NH ₄ Cl	0.4
Na ₂ HPO ₄ ·12H ₂ O	2	KCl	0.5	MgCl ₂ ·6H ₂ O	0.07	FeSO ₄ ·7H ₂ O	0.3	MgCl ₂ ·6H ₂ O	0.2
NaCl	3	FeSO ₄ ·7H ₂ O	0.01	(NH ₄) ₂ SO ₄	0.1	Na ₂ S ₂ O ₃ ·5H ₂ O	0.01	FeSO ₄ ·7H ₂ O	0.01
		NaN ₃	2.5	DMSO ^a	1			Na ₂ S ₂ O ₃ ·5H ₂ O	8
Agar	15	Agar	15	Trace metal sol. (ml) ^b	0.2				
pH	7	pH	7	Agar	15	Gellan gum	5	Agar	15
				pH	7	pH	4	pH	7

^a DMSO, Dimethyl sulfoxide.

^b Trace metal solution (g·l⁻¹), (ethylenedinitrilo)tetraacetic acid disodium salt 50, ZnSO₄·7H₂O 22, CaCl₂ 5, MnCl₂·4H₂O 5, FeSO₄·7H₂O 5, (NH₄)₂MoO₇·2H₂O 1, CuSO₄·5H₂O 1.5, CoCl₂ 1.5

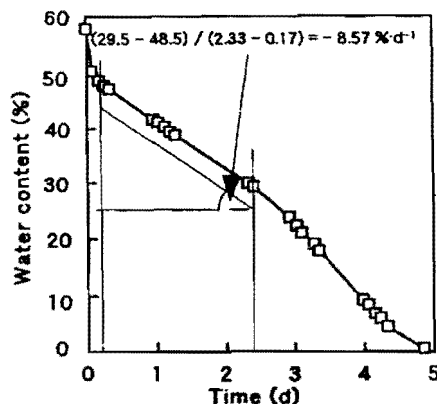


FIG. 2. Time course of water content under flow in packing material A.

extract (NYA) for heterotrophic bacteria, Czapek-Dox agar (CDA) for fungi, dimethyl sulfoxide agar (DMSOA) for *Hypomicrobium* sp., thiosulfate agar (TSA) for less acidophilic sulfur-oxidizing bacteria and modified Waksman gellan gum (MWG) for acidophilic sulfur-oxidizing bacteria. The cell numbers were expressed in colony forming units (cfu). Detailed components of these media are summarized in Table 3.

MLSS measurement of sludge used Sludge was filtered by suction using a cellulose nitrate filter paper (0.2 μm pore size, 47 mm ϕ , Advantec Toyo, Tokyo). Filtered sludge was dried using a filter paper at 100°C overnight and weighed. MLSS was determined as the mean value of three replicate.

H₂S gas The H₂S concentration in cylinders with N₂ as a dilution gas was approximately 20,300 ppm (Takachiho Gas Ltd., Machida, Tokyo). H₂S gas from the gas cylinder was diluted with air to appropriate concentrations.

Gas analysis The H₂S concentration was measured using a gas chromatograph (Shimadzu GC-4BM) equipped with a flame photometric detector and a Teflon column (i.d., 3 mm; length, 6 m) packed with a polyphenyl ether (5 rings) on 60–80 mesh 10% Shimalite TPA. The column temperature, detector temperature and injection temperature were 70, 230 and 130°C, respectively, and N₂ was used as a carrier gas.

RESULTS AND DISCUSSION

Physical and chemical properties of packing materials

The physical and chemical properties of each packing material are summarized in Table 4. Packing materials A and C have higher porosity and maximum water content, and larger mean pore diameter than packing materials B and C. Figure 2 shows the change in water content

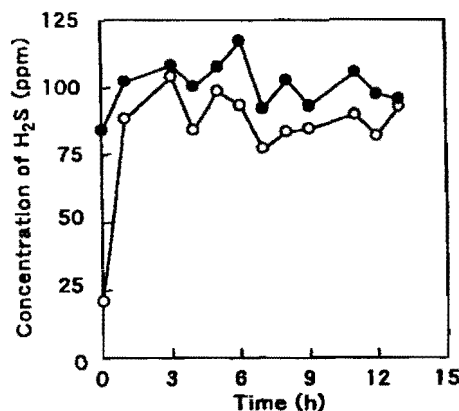


FIG. 3. Nonbiological removal of H₂S under flow in wetted packing material A. Symbols: ●, inlet concentration; ○, outlet concentration.

from the saturated value at a space velocity of 119 h⁻¹ in packing material A. From the decrease in water content on the first day as shown in Fig. 2, 40 ml of water manually supplied to the column daily was sufficient for maintaining the water content of packing materials at 70–80% of maximum water content. Packing materials B, C and D showed the same tendency as that observed in packing material A (data not shown). Water retentivity was calculated from the linear relationship between moisture content and time except for the initial drastic change and was expressed as change in moisture content (% per day). The value for packing material C was the smallest among all the packing materials used (Table 4).

Nonbiological H₂S removal Figure 3 shows the nonbiological H₂S removal in packing material A. The other packing materials used showed a pattern similar to that of packing material A. The nonbiological removal capacity is the amount of net adsorbed gas on packing materials and amount of absorbed gas into free water on packing materials. Nonbiological removal capacities per unit weight and volume of packing material shown in Table 5 were calculated from the difference between the inlet and outlet concentrations. Packing material C has the largest capacity per unit weight, followed by packing material A.

Biological H₂S removal MLSS of sludge used for inoculation was 16 g·l⁻¹, and cell numbers in the sludge were 1.9 × 10⁸, 1.2 × 10⁸, 2.9 × 10⁷, 3.9 × 10⁷ and 1.3 × 10⁷ (cfu·ml⁻¹) as detected on NYA, TSA, MWG, DMSOA and CDA media, respectively. Packing materials were inoculated into the sludge, and then H₂S was supplied to each packing material in a biofilter. Figure 4 shows the time course of H₂S removal patterns in each column. The inlet concentrations and/or space velocity (SV) gradually increased under the same volumetric load of H₂S

TABLE 4. Physical and chemical properties of the packing materials used

Packing material	True density (g·cm ⁻³)	Porosity (%)	Bulk density (g·cm ⁻³)	Pore distribution	Mean pore diameter (μm)	pH	Maximum water content (%)	Water retentivity (%·d ⁻¹)
A	2.31	79.6	0.47	1 μm-less than 100 μm	32.5	6.4	62.8	-8.57
B	1.59	42.6	0.91	mostly in 0.01 μm	0.019	8.2	35.5	-4.39
C	0.13	89.0	0.12	0.1 μm-less than 100 μm	2.32	6.3	89.0	-3.26
D	1.73	46.9	0.92	0.1 μm-less than 10 μm	0.586	7.0	34.0	-6.28

TABLE 5. Amounts of H₂S removed nonbiologically by packing materials under gas flow conditions, and complete H₂S removal capacity and pressure drop in biofilter

Packing material	Nonbiological removal per unit weight (g-S.kg ⁻¹ -dry packing material)	Nonbiological removal per unit volume (g-S.m ⁻³ packing material)	Complete removal capacity per unit weight per day (g-S.kg ⁻¹ -dry packing material.d ⁻¹)	Complete removal capacity per unit volume per day (g-S.m ⁻³ packing material.d ⁻¹)	Pressure drop ^a (mm H ₂ O.m ⁻¹)
A	0.23	57	32.6	3500	6.1
B	0.10	64	2.1	1200	21.7
C	0.36	39	30.9	3400	15.5
D	0.13	50	3.0	1600	31.1

^a Measured at the end of H₂S removal.

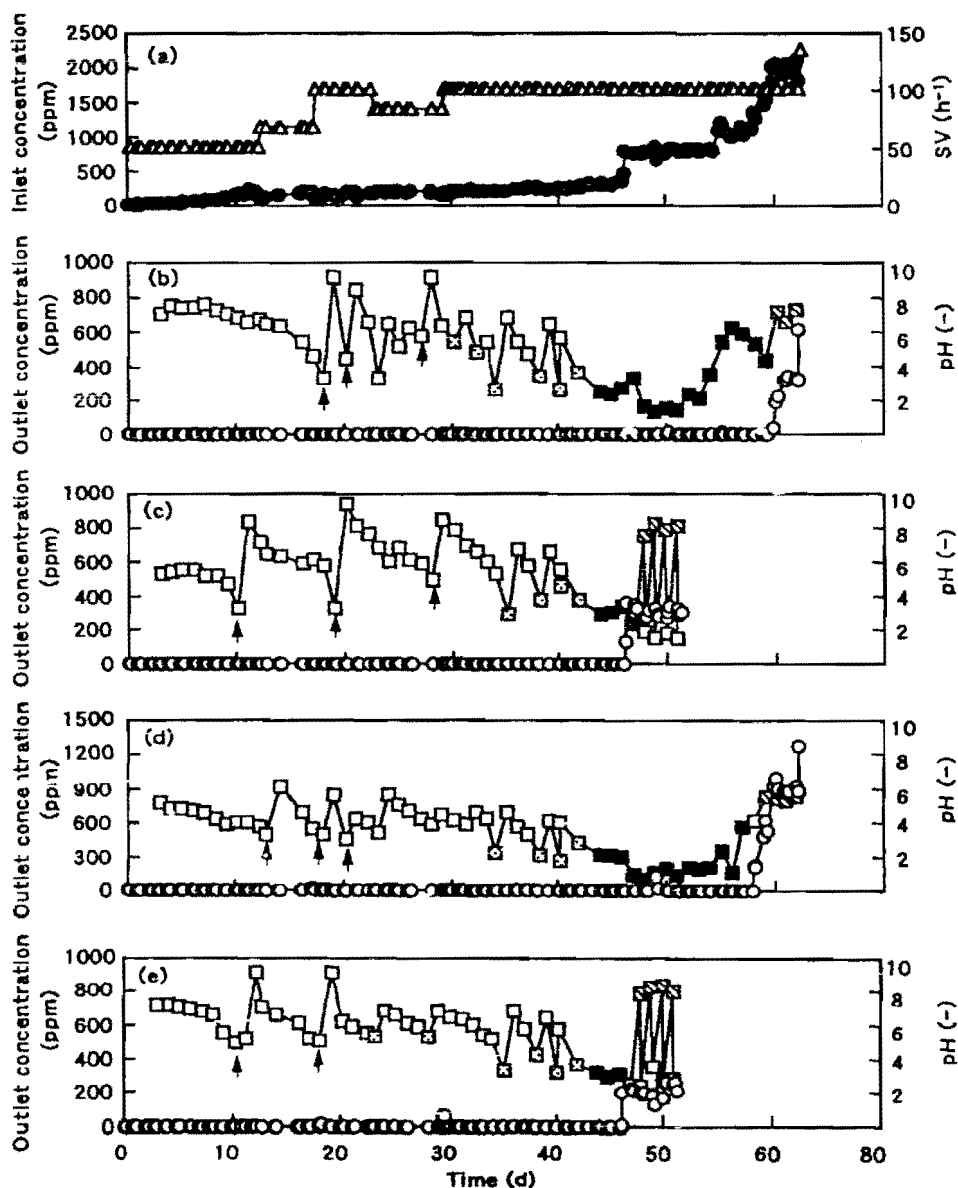


FIG. 4. Time course of biological removal of H₂S and pH change of drain water. Inlet concentration and space velocity (a), outlet concentration of packing material A (b), packing material B (c), packing material C (d) and packing material D (e). Symbols: ●, inlet concentration; △, space velocity; ○, outlet concentration; □, pH of drain water; †, supplied with 36 ml of water and 4 ml of 1% NaHCO₃; ■, washed with 100 ml of water and 40 ml of 0.1% NaHCO₃; ⊞, supplied with 4 ml of 6% HCl.

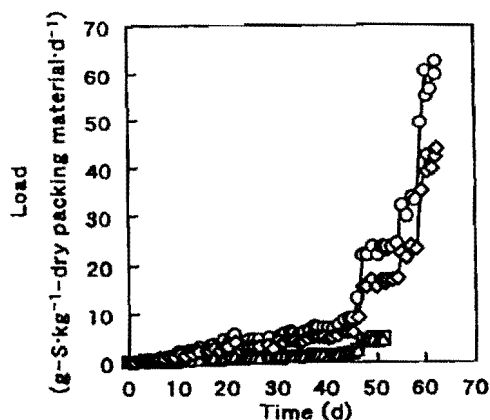


FIG. 5. Time course of H_2S load. Symbols: \diamond , packing material A; \triangle , packing material B; \circ , packing material C; \square , packing material D.

as shown in Fig. 4a. Loads of unit weight packing materials were different in each packing material as shown in Fig. 5 because the bulk density shown in Table 4 is different. Because rapid pH decrease of the drain water due to accumulated H_2SO_4 oxidized from H_2S was observed when excellent removal was achieved, each column was washed with 100 ml of water. Additional supply of water and $NaHCO_3$ solutions to maintain pH at more than 2, which is shown in Fig. 4, was carried out based on the pH of the drain water. Although the pH decrease was observed at the time of supplying 4 ml of 1% $NaHCO_3$ and 40 ml of 0.1% $NaHCO_3$, biological H_2S removal continued even at high H_2S load. After several washings of the accumulated sulfate in each column, the load was increased to obtain the maximum removal capacity in an acclimated biofilter, although H_2S gas was detected in the outlet. During the final period of extremely high H_2S load, a pH increase due to excessive $NaHCO_3$ supply was observed and 6% HCl was added to adjust the pH. A rapid pH increase in the period indicates that no biological H_2S removal occurred. A plot of H_2S -S load versus removal capacity in packing material A is shown in Fig. 6. The diagonal line shows the 100% removal capacity relative to the load. Deviated point from the line gave the complete removal capacity which is summarized in Table 5. Nonbiological removals were temporary phenomena and all of their values were equivalent to biological removal values of less than 1 h. Therefore, they were neglected in calculating the biological removal capacity. Evaluations of packing materials based on H_2S removal per unit weight of packing material and unit volume of packing material per day are in the order of $A \geq C > D \geq B$ and $A > C > D > B$. As a whole, packing materials A and C were better than packing materials B and D in terms of their H_2S removal per unit weight, and packing material A was the

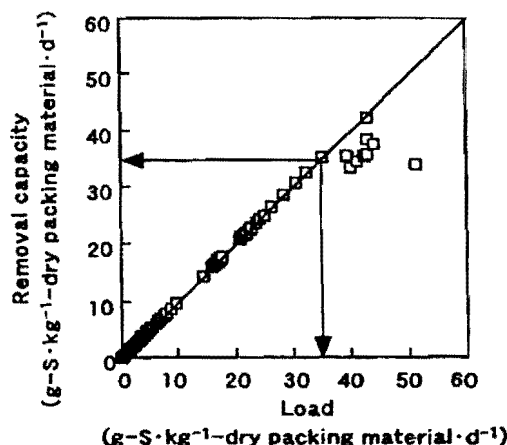


FIG. 6. Plot of H_2S -S load versus removal capacity in packing material A.

best among all in the packing materials used in H_2S removal per unit volume, and subsequently packing material C was good. Pressure drops at the end of H_2S removal are shown in Table 5. Packing material C showed the smallest value. The maximum water content is more closely related to the removal capacity than water retentivity in Table 4. Therefore, frequent supply of water to maintain water content close to the maximum value would improve the removal efficiency of packing material C.

Microbial count Results of microbial counts at the start and end of the flow experiments are summarized in Table 6. Increase in the cell number appeared on TSA, MWG DMSO and CDA, indicating growth of *Thiobacillus* sp. *Hyphomicrobium* sp. and fungi on biofilters. In our previous reports, isolated microorganisms such as *Thiobacillus* sp. and *Hyphomicrobium* sp. in a peat biofilter acclimated by sulfur-containing odorous compounds were ascertained as the dominant species (8, 12, 21, 22). Therefore, similar species would also serve for H_2S removal in the packing materials used. Participation of fungi in H_2S removal was also confirmed (23). No decrease in microbial numbers counted on NYA demonstrates the contribution of heterotrophs in H_2S removal which was shown in a previous paper (24).

Evaluation of H_2S removal characteristics of four packing materials The H_2S removal characteristics of the packing materials used shown in Table 4 are summarized as follows. Packing materials A and B have high true densities. Packing materials C and A have high porosities, lightness and high maximum water contents and are light. Packing material B has high pH. The mean pore diameters of A and C are $32.5 \mu m$ and $2.32 \mu m$, respectively, and those of B and D are very small. Comparison of the H_2S removal characteristics of packing materials A, B, C and D, in terms of biological com-

TABLE 6. Microorganisms acclimated on packing materials under H_2S flow (cfu l^{-1} packing material)

Packing material	NYA		TSA		CDA		MWG		DMSOA	
	Start	End	Start	End	Start	End	Start	End	Start	End
A	1.3×10^{11}	5.7×10^{11}	2.6×10^{10}	3.3×10^{11}	1.6×10^{10}	3.0×10^{11}	2.1×10^9	2.2×10^{11}	1.9×10^{10}	1.4×10^{11}
B	5.4×10^{10}	4.7×10^{11}	1.8×10^{10}	2.7×10^{11}	2.8×10^{10}	2.4×10^{11}	3.2×10^9	2.0×10^{11}	2.6×10^{10}	1.5×10^{11}
C	1.2×10^{11}	3.4×10^{11}	3.8×10^{10}	4.2×10^{11}	1.4×10^{10}	1.6×10^{11}	6.7×10^9	3.8×10^{11}	1.1×10^{10}	2.2×10^{11}
D	7.8×10^{10}	5.0×10^{11}	2.4×10^{10}	2.0×10^{11}	6.8×10^9	1.9×10^{11}	4.3×10^9	1.7×10^{11}	7.7×10^9	2.3×10^{11}

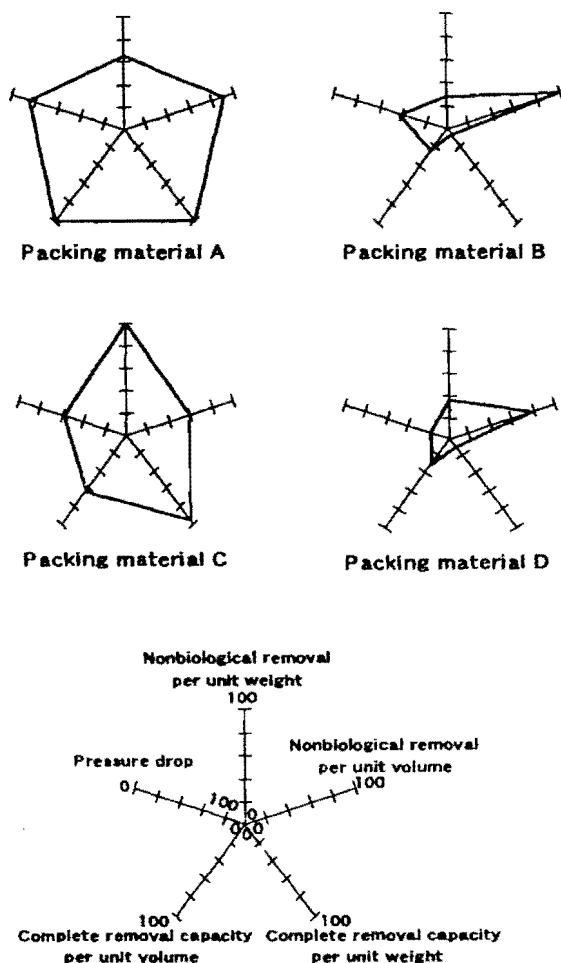


FIG. 7. Overall appraisal as a biological deodorization packing material from the results of H₂S removal experiment on packing materials A, B, C and D. Axis is graduated in relative ratio to the maximal value of all packing materials.

plete removal per unit weight and unit volume, nonbiological removal per unit weight and volume and pressure drop, is shown in Fig. 7 as a radar graph. Each axis is graduated in relative ratios to the maximal value of all packing materials, except for pressure drop which is marked in opposite direction. The price of each packing material is in the order of $A \gg D \approx B \gg C$ (detailed data not shown). Overall appraisal of the packing materials used from the results described above is $A \approx C > D \approx B$ in excellence order. In the removal of acidic H₂S gas, packing materials which have higher pH values are expected to be superior than those with acidic pH values, because of their physical and chemical adsorbing ability. However, in this experiment the pH of the packing materials did not correlate to their removal capacity. The efficient and complete H₂S removal capacity of packing materials A and C is correlated to their physical and chemical properties such as high porosity and mean pore diameter (Table 4). Although there are no differences in cell numbers among the biofilter packing materials at the end of experiment, the differences in physical properties such as porosity, mean pore diameter and maximum

water content contribute to the differences in mass transfer capacity of H₂S, resulting in a different complete H₂S removal capacity of each packing material. In selecting inorganic packing materials for use in biofilters, these physical parameters are important factors for determining the reaction rate between the microorganisms and H₂S.

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