Behaviour and Adsorptive Removal of Siloxanes in Sewage Sludge Biogas

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Behaviour and adsorptive removal of siloxanes in sewage sludge biogas

K. Oshita, Y. Ishihara, M. Takaoka, N. Takeda, T. Matsumoto, S. Morisawa and A. Kitayama

ABSTRACT

We investigated the behaviour of siloxanes, which adversely affect biogas engines, as well as their concentration levels in sewage sludge biogas in Japan. We also performed experiments on the absorptive removal of siloxanes using various adsorbents and determined the main adsorbent characteristics required for the removal of siloxanes. The results of our study on the concentration and composition of siloxanes in biogas were similar to previous reports. Moreover, we found that the concentration of siloxanes changes in relation to the outside air temperature based on real-time measurements of siloxanes using a continuous analyser. We further speculated that the continuous analyser would accurately indicate the siloxane concentration in model biogas but overestimate the siloxane concentration in actual biogas because of positive interference by VOCs and other biogas components. In the siloxane adsorption experiment, the equilibrium uptake of both cyclic siloxanes, D4 and D5, was positively related to the BET-specific surface area of the adsorbents and the fraction of the external surface area taken up by relatively large diameter pores. We attributed the adsorption results to the fact that the siloxane molecules are generally larger than micropores; therefore, they are less susceptible to adsorption to micropores. Based on these results, we concluded that adsorbents with large BET-specific surface areas, especially those with a high external specific surface area and pores of relatively large diameters, are desired for the removal of siloxanes.

Key words | adsorptive removal, BET-specific surface area, external surface area, sewage sludge biogas, siloxane, siloxane continuous analyser

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INTRODUCTION

Anaerobic digestion is a conventional biotreatment process for treating sewage sludge and can stabilise sludge, kill pathogens, and reduce solids. In addition, the biogas produced from sewage sludge can be utilised for the generation of heat and electric power. Biogas produced from sewage sludge is a mixture of CH_4, CO_2, and other minor constituents, such as oxygen, nitrogen, and hydrogen sulfide. Further, it contains various trace constituents, some of which can potentially cause problems during energy recovery operations that involve generating equipment such as gas engines, micro-gas turbines and fuel cells. Therefore, significant attention must be paid to the make-up and concentrations of these trace components when using biogas.

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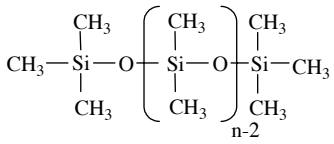
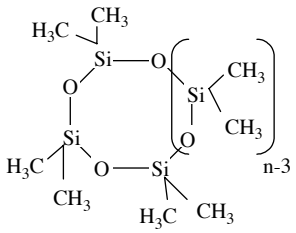
Siloxane is a generic term referring to a subgroup of silicones that contain silanol bonds (Si-O) with methyl and ethyl groups bonded to the silicon atom. Common siloxanes are shown in Figure 1 and Table 1, where L and D are the abbreviations for linear and cyclic siloxanes, respectively, and the number after the L or D denotes the number of silicon atoms. Because of the unique properties of siloxanes, these compounds are used in various industrial processes, e.g., replacing organic solvents, and consumer products, e.g., deodorants, hair and skin care products, lubricants, and water repellents; these products are disposed in wastewater and eventually produce volatile siloxane compounds in biogas (Wang *et al.* 2001). During combustion in a gas engine, siloxanes are converted to silicates and microcrystalline silicon dioxide, which abrade the inner walls of engines and form deposits within the combustion chambers, increasing the cost of engine maintenance (Schweigkofler & Niessner 1999; Prabucki *et al.* 2001; Dewil *et al.* 2005). In addition, the deposits cause accidental explosions by clogging narrow portions of the engines (Takeda *et al.* 2007), and now a siloxane continuous analyser has been developed in Japan (Seki *et al.* 2005); however, few data are available on the presence of siloxanes in biogas in Japan.

Removing siloxanes from biogas upstream of the generating equipment is necessary, and an adsorptive method using activated carbon is the favoured technique for accomplishing this removal (Hagmann *et al.* 2001; Schweigkofler & Niessner 2001). However, many adsorbents other than activated carbon are available, and few



Linear siloxane (Ln)



Cyclic siloxane (Dn)

Figure 1 | The structure of siloxane.

Table 1 | Properties of siloxane (Ito 1990; Kroschwitz 2001; Kochetkov *et al.* 2001; Prabucki *et al.* 2001)

Category	Nomenclature	Abbreviation	Molecular weight	Appearance	Melting point (°C)	Boiling point (°C)	Density (g/cm^3) at 20°C	Refractive index at 20°C	Viscosity (cSt) at 25°C	Solubility (μg/L) at 25°C	Vapour pressure (Pa) at 25°C	Water-octanol partition coefficient LogKow(−)	Henry's constant (−)
Linear	Hexamethyl disiloxane	L2	162.38	Colourless liquid	−68	100	0.7619	1.38	0.63	933	5,613	4.2	397
	Octamethyl trisiloxane	L3	236.53	Colourless liquid	−86	153	0.8200	1.38	1.04	34.5	445	–	–
	Decamethyl tetrasiloxane	L4	310.77	Colourless liquid	−76	194	0.8536	1.39	1.53	6.76	50	–	–
Cyclic	Hexamethyl cyclotrisiloxane	D3	222.46	Colourless crystalline solid	64.5	134	–	–	–	1,563	471	3.85	–
	Octamethyl cyclotetrasiloxane	D4	296.62	Colourless liquid	17.5	172	0.9558	1.40	2.30	56.3	140	4.45	259
	Decamethyl cyclopentasiloxane	D5	370.77	Colourless liquid	−38	210	0.9593	1.40	3.87	17.2	27	5.2	185
	Dodecamethyl cyclohexasiloxane	D6	444.93	Colourless liquid	−3	245	0.9672	1.40	6.62	5.14	3	5.86	104

studies have been performed on the adsorbent characteristics that are most appropriate for the removal of siloxanes.

In the present study, we analysed the adsorptive removal of siloxanes from biogas. First, we investigated the quality and quantity of siloxanes in sewage sludge biogas, according to (1) the batch method of liquid adsorption using hexane and (2) a siloxane continuous analyser, at a sewage treatment plant in Japan. We then evaluated the ability of the siloxane continuous analyser to monitor biogas by comparing the siloxane concentration data from the continuous analyser with concentration data from a GC-MS using model and actual biogas samples. Second, we sought to clarify the adsorbent characteristics that promote the removal of siloxanes. We characterised 10 types of adsorbents that differed in terms of pore structure and chemical composition; we then performed an adsorptive breakthrough experiment on siloxanes produced from model biogas containing D4 or D5 using the siloxane continuous analyser, and we estimated the influence of different adsorbent characteristics on the removal of siloxanes.

EXPERIMENTAL

Materials

As shown in Table 1, we used seven types of siloxanes in this study: L2 (99%), L3 (98%), L4 (97%), D3 (99%), D4 (99%), D5 (99%), and D6 (99%) (all obtained from Shin-Etsu Chemical Co., Ltd, Tokyo, Japan) as reference materials. We used 10 different types of adsorbents for the siloxane adsorption experiment. In particular, we obtained six types of granular activated carbon (AC1–AC6; Dainen Co., Ltd, Hyogo, Japan), silica gel (SG1; Mizusawa Industrial Chemicals Ltd, Tokyo, Japan), and hydrophobic zeolite (Z1) with a high SiO_2/Al_2O_3 ratio (Tosoh Corp., Tokyo, Japan). For synthetic resin adsorbents, we used RS1 and RS2 synthesised from styrene-divinylbenzene copolymer supplied by Mitsubishi Chemical Corp. (Tokyo, Japan). We used n-hexane (minimum purity 96%; Kanto Chemical Co., Inc., Tokyo, Japan) for the sampling and quantitative analysis of siloxanes.

Sampling siloxanes in biogas

Biogas sampling was carried out in a wastewater treatment plant located in Osaka Prefecture in Japan. The average processing capacity of the wastewater treatment plant is 28,000 m^3/day. Sludge generated from wastewater treatment undergoes anaerobic digestion in the mesophilic range after it concentrates; some amount of the resulting biogas is used for generating electricity using a gas engine. We collected the biogas at a sampling tap located just before the gas engine.

The concentrations of CH_4, CO_2, and siloxanes were measured twice a month for a total of eight times. The concentrations of CH_4 and CO_2 were analysed by a gas chromatograph thermal conductivity detector (GC-TCD) (G-1001A; Yanagimoto Corp., Kyoto, Japan) after collecting the biogas in a gas bag.

The flow of siloxane was adjusted to 1 L/min using a suction pump, and approximately 15 L of biogas were circulated through the wet sampling equipment for 15 min for each measurement. In the wet sampling equipment, three 150-mL impingers were connected in series. The first impinger was empty, while the second and third impingers were filled with a total of 200 mL of n-hexane (minimum purity 96%; Kanto Chemical Co.). All three impingers were chilled with ice. The integrated gas volume was measured using a dry gas meter (DC-1; Shinagawa Co., Ltd, Tokyo, Japan). After sampling, the concentrations of the seven types of siloxanes present in the collected liquid were directly measured in the laboratory by GC/MS (HP6890/HP5973; Hewlett Packard Co., Ltd, Palo Alto, CA, USA) without pre-treatment of the collected liquid sample. In addition, real-time measurement of the concentration of siloxanes was performed by bifurcating a sampling line of biogas and circulating the biogas at a rate of 0.5–0.8 L/min through a siloxane continuous analyser (VA-3001S; Osaka Gas Engineering Co., Ltd, Osaka, Japan).

GC-MS analysis

The following conditions were used to measure the seven types of siloxanes by GC/MS (HP6890/HP5973; Hewlett Packard). The carrier gas was helium and was supplied at a constant flow rate of 1 mL/min. We used an HP-5MS (Hewlett Packard) capillary column (length: 60 m, inner diameter: 0.250 mm, film thickness: 0.25 μm). The GC-MS was carried out in a selected ion monitoring (SIM) mode, and the molecular ion of each compound was scanned at a

rate of 1.5–2.0 scans/s. The inlet and interface temperatures were maintained at 230°C and 280°C, respectively. The column temperature was initially held at 40°C for 4 min and was then increased to 100°C at a rate of 6°C/min and then to 200°C at 4°C/min. Finally, the column was heated to 280°C at a rate of 30°C/min, and its temperature was maintained at 280°C for 3 min.

Siloxane continuous analyser

A siloxane continuous analyser (VA-3001S; Osaka Gas Engineering Co., Ltd) was used to measure the Si-O and Si-CH_3 bonds (1150–1000 and 850–770 cm^{-1}, respectively), which are always present in a siloxane molecule, by infrared spectroscopy. These bonds were measured to determine their quantity in a D4 equivalent amount (ppmv). Moreover, while measuring the concentration of CO_2 by infrared spectroscopy, gas flowing into the analyser was cooled to 5°C using a pre-treatment system (PS-200S, Horiba, Ltd, Kyoto, Japan), and measurements were performed with a fixed amount of moisture by dehumidification, which offset the interference to the siloxane measurements caused by CO_2 and moisture. We performed real-time measurements at intervals of 1 min and recorded the values on a laptop. To calibrate the analyser, we used N_2 gas (ZERO-A; Sumitomo Seika Chemicals Co., Ltd, Osaka, Japan) as a zero calibration gas and D4 standard gas ($C_8H_{24}O_4Si_4$, 42.5 ppmv/N_2; Sumitomo Seika Chemicals Co.) as a span calibration gas. Simultaneously, using a K thermocouple we measured the air temperature of the gas engine room in which the analyser was installed and recorded it on the laptop.

Properties of adsorbents

We studied the properties of the 10 types of adsorbents used in the siloxane adsorptive breakthrough experiment. We measured parameters such as ash content, total carbon (TC), bulk density, BET-specific surface area, micropore surface area, total pore volume, and average pore diameter. The ash content was measured using JIS K1474 (JIS 2007). TC was measured using a total organic carbon analyser (TOC-V_{CSH}; Shimadzu Corp., Kyoto, Japan) based on a dry combustion method and a solid sample combustion unit (SSM-5000A; Shimadzu Corp.). Bulk density was measured using JIS Z 8807, while the BET-specific surface area, micropore surface area, total pore volume, and average pore volume were analysed by determining the adsorption isotherm of nitrogen using a nitrogen adsorption isotherm measurement device (ASAP2020; Micromeritics, Norcross, Georgia, USA). Micropore surface area was measured using a t-plot method (Mikhail *et al.* 1968).

Siloxane adsorptive breakthrough experiment

We used the experimental setup shown in Figure 2 for the adsorptive breakthrough experiment. The siloxanes D4 and D5 were used in the adsorptive breakthrough experiment. First, we placed an impinger filled with reference solutions of D4 and D5 (99%; Shin-Etsu Chemical Co.) in a water bath; the temperatures of the D4 and D5 were maintained at 0°C and 10°C, respectively. Next, we passed nitrogen gas (ZERO-A; Sumitomo Seika Chemicals Co.) through the impinger and created a model gas with a random concentration. In this case, the concentrations of D4 and D5 were 46 ± 2 ppmv and 21 ± 2 ppmv, respectively. We adjusted the mass flow controller (Kofloc, MC-1A; Kojima Instruments Inc., Kyoto, Japan) such that the model gas would be created at a rate of 1 L/min.

We maintained the temperature of the constant temperature oven (LL-75; GL Sciences Inc., Tokyo, Japan) at 27 ± 1°C and prepared two columns (17 mmφ × 250 mm) made of glass, which were filled with adsorbents. Column A was prepared for measuring the concentration flowing into the adsorbents, without filling it with adsorbents. Using a sieve (JIS 2006), we prepared 10 types of adsorbents such that the grain diameter would be 0.85–2.0 mm. We filled column B with 0.5 ± 0.005 g of adsorbents and firmly

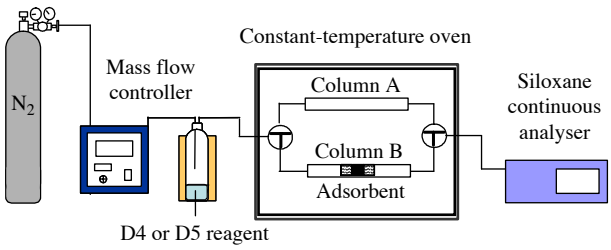


Figure 2 | Setup of the adsorptive breakthrough experiment.

closed it with 0.1 g of glass wool. The entire gas flow path for the experimental setup was made of glass or Teflon.

After starting the experiment, we circulated the model gas through column A, measured the concentration of siloxanes using the siloxane continuous analyser (VA-3001S; Osaka Gas Engineering Co., Ltd), and verified that the concentration of siloxanes stabilised at a prescribed concentration. Next, by operating a three-way cock, we circulated the model gas through column B and measured the concentration of siloxanes in the gas at the outlet of the adsorbents using the continuous analyser. We recorded the concentration of siloxanes until it became equal to the concentration of siloxanes in the gas at the inlet of the adsorbents; we then plotted the adsorption breakthrough curve. By analysing this curve, we determined the equilibrium adsorption amount of D4 and D5 for each adsorbent.

RESULT AND DISCUSSION

Siloxanes present in biogas

The results of the biogas composition analyses are listed in Table 2. The mean values of the concentrations of CH_4 and CO_2, the main constituents of biogas, were 60.9 Vol. % (standard deviation: 2.48 Vol. %) and 40.1 Vol. % (standard deviation: 4.84 Vol. %), respectively, which are very similar to the general composition of biogas.

Table 2 | Siloxane concentrations in biogas (CH_4, CO_2; Vol. %, Siloxane: mg/m^3_N)

Item	Concentration	S.D.
CH_4	60.9	2.48
CO_2	40.1	4.84
Siloxane		
L2	<0.6	–
L3	<0.6	–
L4	<0.6	–
D3	0.66	0.12
D4	6.1	2.4
D5	25.5	11.4
D6	<0.6	–
Total	32.2	13.2

S.D.: Standard deviation; Siloxane level of determination: 0.6 mg/m^3_N.

The levels of the linear siloxanes L2, L3, and L4 and the cyclic siloxane D6 were below detection limits; D3, D4, and D5 were detected at average concentrations of 0.66, 6.1, and 25.5 mg/m^3_N, respectively. From this result, we concluded that most of the siloxanes present in biogas are cyclic and that D4 and D5 are the main constituents. Schweigkofler & Niessner (1999; 2001) also reported that the main constituents of siloxanes present in biogas are D4 and D5, at concentration ranges of 2.9 to 8.2 mg/m^3_N and 2.8 to 15.5 mg/m^3_N, respectively. These levels of D4 were more or less within the same range as our findings, but those of D5 were somewhat lower than our results. However, with a total concentration of siloxanes of 32.2 mg/m^3_N, our results are in agreement with the total siloxane (primarily D4 and D5) concentration of approximately 20–60 mg/m^3_N reported by Dewil *et al.* (2005).

In preparation for the real-time measurements by the siloxane continuous analyser, we compared the D4 and D5 concentrations in model gas analysed by the continuous analyser with those concentrations indicated by the GC-MS using the experimental setup shown in Figure 2. The relationship between the D4 and D5 concentrations measured by these two methods is shown in Figure 3a. The D4 concentrations showed a one-to-one relationship, but the D5 concentrations indicated by the continuous analyser were 1.26 times higher than those measured by the GC-MS. This discrepancy was attributed to the fact that the D5 concentrations indicated by the continuous analyser are in a D4 equivalent amount, and the Si-O and Si-CH_3 bonds in one D5 molecule are 1.25 times as prevalent as in one D4 molecule. Therefore, we converted cyclic siloxane concentrations in D4 equivalent amounts analysed by the continuous analyser to concentrations analysed by the GC-MS using Equation (1).

$$C_{\mathrm{Dn-MS}} = C_{\mathrm{Dn-SCA}} \cdot \left(\frac{4}{n}\right) \quad (1)$$

where n is the number of Si atoms in a Dn siloxane molecule ($n = 3$–6), $C_{\mathrm{Dn\text{-}MS}}$ is the Dn concentration analysed by GC-MS (ppmv), and $C_{\mathrm{Dn\text{-}SCA}}$ is the Dn concentration in a D4 equivalent amount analysed by the continuous analyser (ppmv).

The siloxane concentrations in the actual biogas analysed by the continuous analyser were then compared

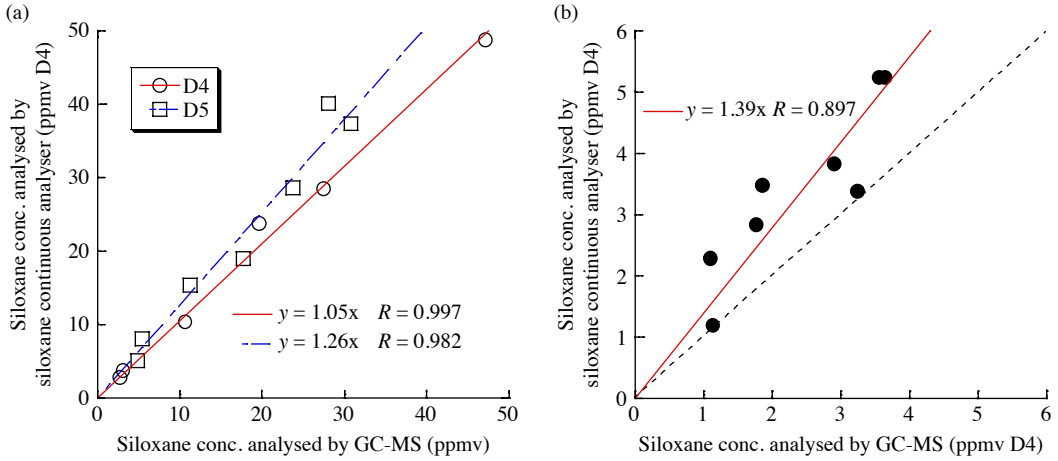


Figure 3 | Relationship between the siloxane concentrations analysed by GC-MS and the siloxane continuous analyser (a) in the model biogas and (b) in the actual biogas.

with the concentrations analysed by the GC-MS (Figure 3b). The siloxane concentrations analysed by the GC-MS were converted to D4 equivalent concentrations using Equation (1) and showed a high correlation. But the siloxane concentrations indicated by the continuous analyser remained higher than those calculated by the GC-MS measurement and Equation (1). The reason for this correlation is that the continuous analyser measures the Si-CH_3 bonds (850–770 cm^{-1}) by infrared spectroscopy, and the = C-H bonds (Silverstein *et al.* 1981) in trace VOCs (Schweigkofler & Niessner 1999; Ho-Chul Shin *et al.* 2002) found in actual biogas have an infrared absorption peak around 850–770 cm^{-1}, which causes positive interference.

The time-series trend of siloxane concentration (D4 equivalent), outside air temperature, and CO_2 concentration measured using the siloxane continuous analyser was then evaluated for a period of 5 days (Period A) as shown in Figure 4a. Although the outside air temperature fluctuated between 5°C and 15°C over a period of 1 day, the CO_2 concentration was stable at approximately 35 Vol. % However, along with the changes in temperature, the siloxane concentration ranged from 0.6 to 3.7 ppmv over a period of 1 day. The relationship between the outside air temperature and the siloxane concentration for two periods (Periods A and B) is shown in Figure 4b. In this figure, a certain amount of correlation between the total siloxane concentration and the outside air temperature

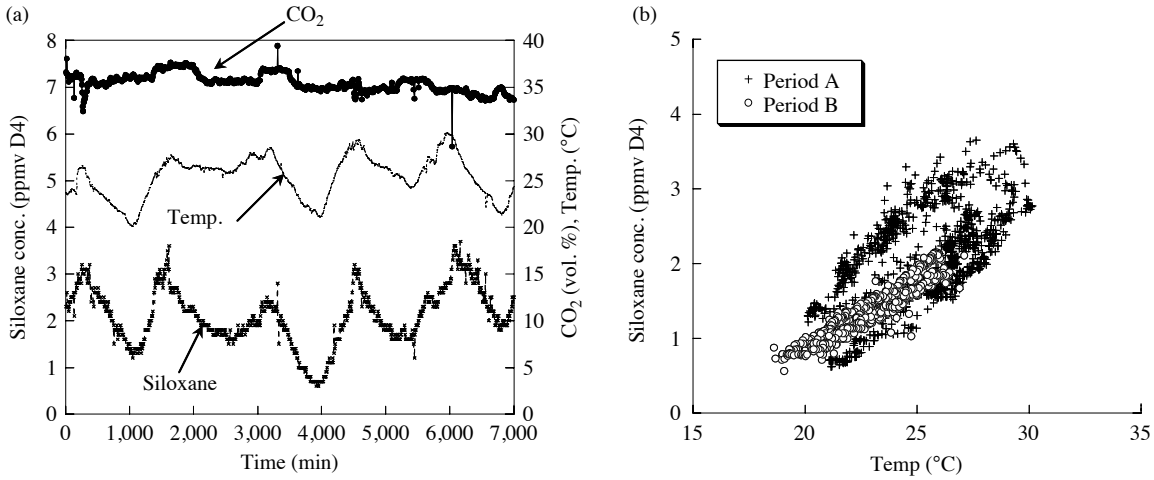


Figure 4 | Temperature, siloxane concentration, and CO_2 concentration in biogas analysed by the siloxane continuous analyser (a), and the relationship between temperature and siloxane concentration in biogas (b).

Table 3 | Characteristics of the adsorbents

Unit	Ash content wt%	TC wt%	Bulk density g/ml	BET-specific surface area: S_{BET} m^2/g	Micropore surface area: S_M m^2/g	S_M/S_{BET} %	External surface area: S_E m^2/g	Total pore volume cm^3/g	Average pore diameter Nm
AC1	6.5	91.3	1.54	1,080	432	40	644	0.541	2.01
AC2	7.0	88.7	1.49	980	510	52	470	0.507	2.07
AC3	6.6	88.0	1.06	650	532	82	118	0.346	2.13
AC4	6.5	91.7	1.24	1,060	449	42	613	0.808	3.04
AC5	5.6	86.3	1.24	1,100	856	78	240	0.553	2.02
AC6	12.6	71.7	1.52	1,370	334	24	1,040	0.940	2.75
SG1	92.1	0.6	2.11	717	233	33	484	0.376	2.10
Z1	99.1	N.D.	2.17	712	569	80	143	0.506	2.85
RS1	0.0	90.4	1.01	936	–	–	1,080	1.480	6.30
RS2	0.0	93.1	1.04	765	108	14	657	0.933	4.88

N.D.: Not detected.

can be observed. The saturated vapour pressures of D4 and D5 at 25°C are 140 Pa and 27 Pa, respectively (Dewil *et al.* 2005). In this study, we calculated the concentrations of D4 and D5 as approximately $1/10^4$ and $1/10^2$ of the saturated concentration. Condensation of D4 and D5 due to low relative pressure is unlikely. Schweigkofler & Niessner (1999) pointed out that, when biogas is directly collected in a stainless steel container, siloxanes with a high polymerisation degree and low boiling point adsorb to the internal wall of the container. Similarly, in this case, biogas generated from the digestion chamber and kept at a mesophilic range of 35–37°C cools down when the outside air temperature is less than 30°C. During this cooling process, some of the siloxanes present as gas may adsorb to the inner surface of the gas pipe or gasholder. Therefore, we inferred that siloxanes remain in equilibrium relative to the outside air temperature.

Characterisation of adsorbents

Table 3 lists the measurement results of carbon content, TC, bulk density of adsorbents, and BET-specific surface area (S_{BET}) of the pore structure. The BET-specific surface area was 650–1,370 m^2/g for activated carbons (AC1–AC6), 717 m^2/g for silica gel (SG1), 712 m^2/g for zeolite (Z1), and 936 and 765 m^2/g for the synthetic resin adsorbents (RS1 and RS2, respectively). The micropore surface area (S_M) determined by the t-plot method was 334–856 m^2/g for activated carbons (AC1–AC6), 233 m^2/g for silica gel (SG1), 569 m^2/g for Z1, and 108 m^2/g for RS2. The micropore surface area could not be measured for RS1. S_M/S_{BET} is the ratio of the micropore surface area to the BET-specific surface area. The S_M/S_{BET} of AC3, AC5 and Z1 were 78–82% and higher than those of other adsorbents. We inferred that micropores with pore diameters less than 2.0 nm develop in these adsorbents. The total pore volume was in the range of 0.346 to 1.475 cm^3/g for all adsorbents. Moreover, the average pore diameter was in the range of 2.02 to 3.04 nm, except for the two types of synthetic resin adsorbents. As the average pore diameters of RS1 and RS2 were high, i.e., 6.30 and 4.88 nm, respectively, and the S_M/S_{BET} ratio was low, we inferred that pores of relatively large diameters developed in these adsorbents.

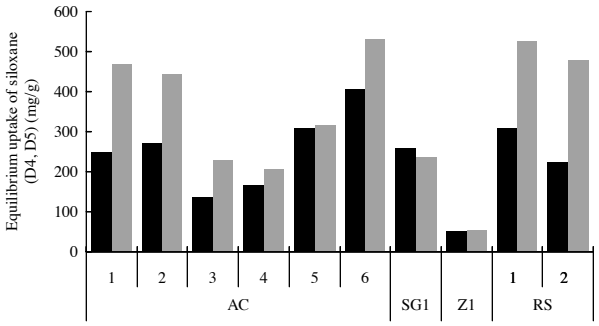


Figure 5 | Equilibrium uptake of siloxane (D4, D5).

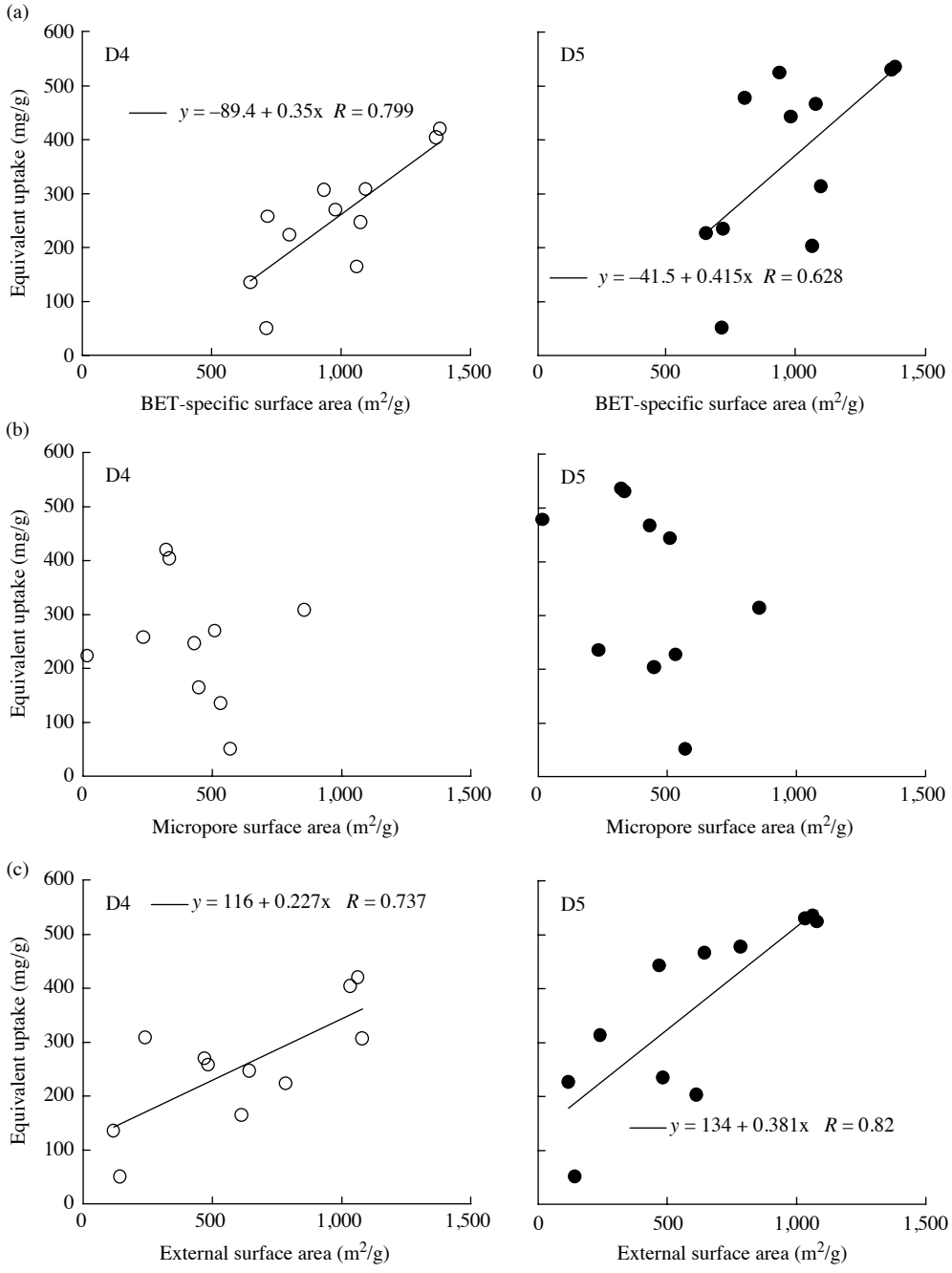


Figure 6 | Relationship between equivalent uptake of siloxane (D4 and D5) and (a) BET-specific surface area, (b) micropore surface area, and (c) external surface area.

Results of the siloxane adsorptive breakthrough experiment

Figure 5 shows the equilibrium uptake for 10 types of adsorbents when 46 ppmv of D4 and 21 ppmv of D5 were circulated through. The equilibrium uptakes of both D4 and D5 were the highest for AC6 at 404 mg/g and 531 mg/g, respectively. The equilibrium uptakes of both D4 and D5 were the lowest for Z1 at 51 mg/g and 52 mg/g, respectively. In general, adsorbents with high equilibrium uptakes of D4 also had high equilibrium uptakes of D5 compared to other

adsorbents. This indicated that the adsorption behaviours of D4 and D5 were similar.

Moreover, the adsorbents selected in this study, such as Z1, SG1, and AC1–C6, had varied chemical compositions. Accordingly, their equilibrium uptakes also differed. However, the equilibrium uptakes even varied among the activated carbons, which had similar chemical compositions. Therefore, we inferred that differences in the adsorption characteristics are due to the different pore structures of the adsorbents.

Consequently, we studied the relationship among the equilibrium uptakes of D4 and D5, total pore volume, BET-specific surface area (S_{BET}), micropore surface area (S_M), and external surface area (S_E) where $S_{BET} = S_M + S_E$, as some of the parameters of the pore structure of the adsorbents.

The relationships between the BET-specific surface area of the adsorbents and the equilibrium uptakes of D4 and D5 are shown in Figure 6a. A positive correlation between the two can be observed in this figure. The correlation coefficients of D4 and D5 were 0.8 and 0.63, respectively. We also observed that siloxanes adsorb to adsorbents with large specific surface areas, irrespective of chemical composition. Moreover, the correlation tended to be higher for D4.

Hardly any correlation was observed between the micropore specific area of adsorbents and equilibrium uptakes of D4 and D5, as shown in Figure 6b. Although we inferred that micropores developed in AC3 and AC5, their equilibrium uptakes of D4 and D5 were 135–309 and 228–315 mg/g, respectively; this result did not differ from the equilibrium uptakes of the other adsorbents. Thus, we concluded that micropore surface area does not substantially contribute to the adsorptions of D4 and D5.

The relationships between the external surface areas of the adsorbents and the equilibrium uptakes of D4 and D5 are shown in Figure 6c. A positive correlation between the two can be observed in this figure. The correlation coefficients of D4 and D5 were 0.74 and 0.82, respectively, indicating that the equilibrium uptakes of D4 and D5 were correlated with the BET-specific surface area and also related to external surface area. We determined the micropore surface area by analysing the adsorption isotherm of N_2 using a micropore distribution measurement device (ASAP2020; Micromeritics); considering that the micropore diameter is between 0.35 and 2.0 nm (size of a nitrogen molecule), we can infer that D4 and D5 would tend to adsorb to even pores with diameters larger than 2.0 nm. Assuming that the molecular area of D4 is 1.08 nm × 1.03 nm (Hamelink *et al.* 1996) and that the molecular volumes of D4 and D5 are 309.2 and 386.5 cm^3/mol (Kochetkov *et al.* 2001), respectively, we can infer that the molecular volume of D5 is larger than that of D4. Although D4 and D5 may also adsorb to micropores with diameters less than 2.0 nm, they are then less likely to adsorb to internal surfaces of micropores than when adsorbed to pores of diameters greater than 2.0 nm. Moreover, no significant correlation was observed between total pore volume, average pore diameter, and equilibrium uptakes of D4 and D5.

The selection of an adsorbent with a large adsorptive capacity is important for the removal of siloxanes. From the above results, we can conclude that adsorbents with large BET-specific surface areas, especially those with high external surface areas and relatively large diameter micropores, are desired.

CONCLUSIONS

We investigated the behaviour of siloxanes, which can adversely affect biogas engines, as well as their concentrations in biogas used in Japan. We also experimentally examined the adsorptive removal of siloxanes using various adsorbents and determined the main adsorbent characteristics required for the removal of siloxanes. The results of our study on the concentrations of siloxanes in biogas were similar to previously reported data. We also found that D4 and D5 were the main types of siloxanes and that their concentration ranges were similar to those reported by other researchers. Moreover, real-time measurements of siloxanes performed for a period of approximately 5 days using a siloxane continuous analyser indicated that the concentration of siloxanes varies with the outside air temperature. This association may be caused by the fact that some of the siloxanes that exist as gas when generated adsorb to the internal surface of the gas pipe or the gas holder. Therefore, we inferred that the equilibrium condition was maintained with respect to the outside air

temperature. Our data suggest that the siloxane continuous analyser could accurately analyse the siloxane concentration in model biogas, but would likely overestimate the siloxane concentration in actual biogas because of positive interference by VOCs and other components.

In the siloxane adsorptive experiment, we found that the equilibrium uptakes of both D4 and D5 increased in relation to the BET-specific surface area of the adsorbent and the extent of external surface area contributed to by relatively larger diameter pores. We attributed these findings to the fact that the siloxane molecules are comparatively larger than most micropores; therefore, siloxanes are less susceptible to adsorption by micropores. Based on these results, we concluded that adsorbents with large BET-specific surface areas, especially those with a high external specific surface area and pores of relatively larger diameters, are desired for the removal of siloxanes. However, in actual biogas, moisture, VOCs (Schweigkofler & Niessner 1999; Ho-Chul Shin *et al.* 2002), and other parameters compete with D4 and D5 for adsorption, and VOCs might interfere in the analysis of siloxanes by a continuous analyser. Thus, to optimise biogas engine performance, it is essential to clarify the effects of these coexisting materials.

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