

Removal of siloxanes in biogases

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Abstract

Methods for the removal of gaseous silicon compounds in biogases are presented. In laboratory studies, various solid adsorption materials and liquid absorption solutions were evaluated for their siloxane elimination efficiencies. Among the liquid sorbents studied, concentrated nitric acid and sulfuric acid were found to be especially potent siloxane removing agents at elevated temperature. Solid adsorbents tested include activated charcoal, carbopack B, Tenax TA, XAD II resins, molecular sieve 13X and silica gel. Apart from activated charcoal, silica gel showed especially high adsorption capacities of more than 100 mg/g for siloxanes. Furthermore, excellent thermal regeneration of the loaded material was possible. The efficiency of silica gel in removing gaseous siloxanes was verified at a sewage treatment plant, where an adsorption bed with silica gel was used for biogas drying. Other gas pretreatment installations studied included refrigeration condensers and adsorbent beds of meadow ore for the catalytic removal of hydrogen sulfide. In contrast to biogas drying by refrigeration, which had a poor effect on siloxane content, the installation of meadow ore adsorption beds resulted in a significant siloxane reduction of 31–75%, depending on the site studied. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

1.1. Biogas

Biogas produced by the digestion of organic materials in waste disposal sites and sewage treatment plants has to be collected and combusted [1]. Since it contains about 50–65% by volume methane this process yields energy. The major nonmethane constituent of biogas is carbon dioxide with a typical concentration of 30%. Landfill gas may further contain nitrogen and oxygen, which are indicative of air incursion into the gas collection system [2]. Oxygen concentrations are monitored continuously and held low for safety reasons.

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Apart from the main components mentioned, landfill gas and sewage gas contain a variety of trace compounds. More than 140 substances have been identified so far and they reach a total concentration of up to 2000 mg/m^3 (0.15 vol.%) [3]. When biogas is used as a fuel for electricity generation, several trace compounds may damage the combustion engines, requiring expensive repairs and causing service interruptions. Specific contaminants to biogas utilization are hydrogen sulfide, halides and silicon containing compounds. During the combustion process, hydrogen sulfide and halogenated compounds form corrosive acids like H_2SO_4 , HCl and HF [4]. Siloxanes are converted into silicates and micro-crystalline quartz, which contribute to abrasion of the inner surfaces within the combustion engine [5]. In our own measurements of landfill gas silicon compounds (trimethylsilanol, hexamethyldisiloxane L2, octamethyl-trisiloxane L3, decamethyltetrasiloxane L4, hexamethylcyclotrisiloxane D3, octamethylcyclo-tetrasiloxane D4, decamethylcyclopentasiloxane D5 and dodecamethylcyclohexasiloxane D6) in concentrations of up to 50 mg/m^3 were found. These concentrations are far beyond the limit of 15 mg/m^3 imposed by several engine manufacturers and a gas pretreatment is highly recommended.

1.2. Gas pretreatment systems

The removal of harmful trace constituents in biogases is achieved by both wet and dry contacting techniques. Usually, the first step in gas pretreatment consists of the reduction of water vapor by a refrigeration condenser. This gas drying enhances the effectiveness of the downstream adsorbent beds or absorption columns, and simultaneously the bulk of the heavier hydrocarbons is removed from the biogas [6]. The most common adsorbent material for the removal of halides and hydrogen sulfide is activated charcoal. To improve the adsorption capacity for hydrogen sulfide, it can be impregnated with potassium iodide [7]. In some cases, activated charcoal is also used to reduce silicon content, but since siloxanes are difficult to desorb from the material, these adsorbent beds have to be replaced regularly. Other adsorbents used for the removal of gaseous siloxanes include molecular sieves and polymer beads [8]. To enable gas purification without interruption, two beds are used in parallel. During operation, one bed is adsorbing while the parallel bed is being regenerated. An elegant method for the regeneration of the adsorbents is the use of hot exhaust from the fuel cell or of heated pretreated raw gas. The regeneration gas loaded with the organic trace compounds is added to the exhaust or may be fed into a separate incinerator where it is combusted. The latter method is advantageous since emissions of halides and VOCs into the atmosphere are avoided.

Another approach for the removal of gaseous siloxanes is physical absorption using high boiling organic solvents. Installations for siloxane absorption include both spraying devices and columns with packings like Raschig rings [9,10]. A major drawback of this gas pretreatment method is the fact that complete silicon elimination is difficult to obtain since the highly volatile siloxanes are stripped from the solvent at elevated gas flow rates. This problem does not arise if the siloxanes are absorbed chemically, i.e. they are converted to compounds of low volatility.

In this study, several liquid and solid materials were evaluated for their siloxane elimination efficiency. Furthermore, gas pretreatment installations at different landfill sites and sewage treatment plants were studied with regard to their siloxane removing potential.

2. Experimental

2.1. Materials

Volatile siloxanes used as standards and for spiking purposes were D5 (97%, Gelest, Karlsruhe/Germany), D4 (99%), D3 (98%) and L2 (99.5%, all from Aldrich, Steinheim/Germany). Silica gel was obtained from Fluka (Deisenhofen/Germany), activated charcoal was from Merck (Darmstadt/Germany), all other adsorbent materials (molecular sieve 13X, XAD-II resins, Tenax TA, Carboxpack B) were obtained from Supelco (Deisenhofen/Germany). Dodecane and hexadecane used for the physical absorption of siloxanes were both of 99% purity (Aldrich, Steinheim/Germany), further liquids used for chemical absorption experiments include sulfuric acid (95–97%), nitric acid (65%), and phosphoric acid (85%, all from Merck, Darmstadt/Germany).

2.2. Gas chromatographic system

A Hewlett Packard 5890 series II gas chromatograph with a fused silica capillary column and a FID was used and programmed as follows: 40°C 2 min isothermal, 25°C/min to 250°C, 5 min isothermal at 250°C. The other conditions were as follows: carrier gas, nitrogen; linear gas velocity, 53 cm/min; injector temperature, 250°C; detector temperature, 300°C; injection volume, 1 µl splitless; column, DB-5; film thickness, 0.25 µm; 30 m × 0.32 mm i.d.

Biogas samples were analyzed using a Hewlett Packard 5890 series II gas chromatograph, coupled to a mass selective detector (HP 5971 A) and an atomic emission detector (HP 5921 A), which were operated in parallel. The GC system was further equipped with a thermal desorption unit (Tekmar 6000), a canister module (Tekmar Aerocan) and a cryofocusing module (Tekmar). Individual substances were identified independently by both MSD analysis and based on their elemental constitution. Quantification of trace compounds was achieved using a 30 component external standard containing siloxanes and VOC. Further information on the entire analytical system is given elsewhere [11].

2.3. Siloxane test gas

For the generation of siloxane test gas an experimental set-up as depicted in Fig. 1 was used. A metered nitrogen gas stream (flow 1) was passed over the surface of the tempered pure siloxane (L2 or D5) and diluted with a second nitrogen flow (flow 2) in a ring gap mixing nozzle. The siloxane concentration was adjusted to 1 g/m³ (4 g/m³ in experiments involving silica gel), the final test gas flow rate was 200 ml/min. Experimental parameters for each siloxane test gas are given in Table 1. To determine the exact siloxane concentration, the test gas was bubbled through a gas washing bottle filled with 20 ml of organic solvent (dodecane for experiments with L2, hexadecane for D5 experiments) which was proved to absorb siloxanes quantitatively under the given conditions. Aliquots of the solvent (0.2 ml) were taken regularly and analyzed by GC/FID. For quantification purposes the solvents were spiked with the siloxanes D3 and D4, respectively.

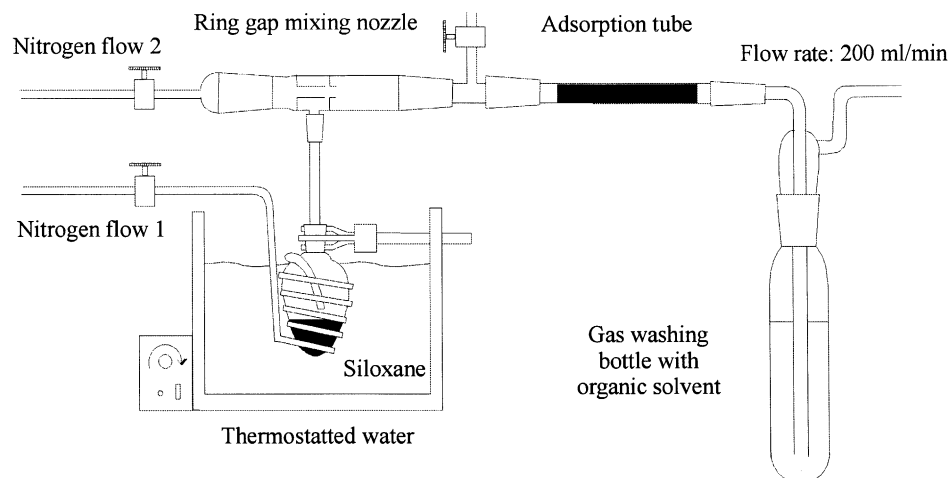


Fig. 1. Experimental set-up for test gas generation and adsorption/absorption experiments.

2.4. Adsorption and absorption experiments

To determine the siloxane adsorption capacity of different solid sorbent materials, the siloxane test gas was led through an adsorption tube (120 mm × 5 mm i.d.) packed with 500 mg of sorbent material (see Fig. 1). The escaping siloxane was absorbed in 20 ml of organic solvent which was analyzed regularly by GC-FID. To avoid adsorption of siloxanes on nonpolar surfaces, the entire apparatus was made of glass. For absorption experiments, the adsorption tube was displaced by a 250 ml gas washing bottle filled with 50 ml of absorbing solution.

2.5. Sampling procedure of biogases

Two sewage treatment plants in Munich and one waste disposal site in Augsburg were sampled. Raw biogas and treated biogas samples were collected directly into evacuated 15 l stainless steel canisters (Tekmar) using tubing (Tygon[®]) as short as possible.

Table 1
Parameters for the generation of siloxane test gases

Siloxane	Temperature (°C)	Flow 1 (ml/min)	Flow 2 (ml/min)	Test gas flow (ml/min)	Test gas concentration (g/m ³)
L2	20	100	2700	200	1.1–1.3
L2	20	100	700	200	4.0–4.4
D5	20	300	100	200	1.0–1.2
D5	40	300	0	200	3.8–4.3

Table 2
Eco-relevant properties of silicon compounds found in biogases [14]

	Boiling point	Vapor pressure at 25°C (mmHg)	Water solubility at 25°C (mg/l)	log K_{ow}
Trimethylsilanol	69.5	16.0	35000	1.14
L2	106.9	42.2	0.93	4.2
D3	135.2	8.6	1.56	3.85
D4	175.7	0.99	0.056	4.45
D5	211.2	0.174	0.017	5.2
D6	245.1	0.03	0.005	5.86

3. Results and discussion

3.1. Siloxane elimination by gas–liquid extraction

Cyclic and linear (dimethyl)siloxanes are very stable against chemical and biochemical degradation. However, strong acids or bases catalyze the cleavage of Si–O bonds to give poly(dimethyl)siloxanes (silicones) [12]. Due to the high content of CO₂ in biogases, the application of caustic absorbents for siloxane removal is not practicable, since large amounts of carbonates formed may pose problems due to precipitation in the absorption unit [13]. Thus, only acidic solutions were evaluated for their efficiency in siloxane removal. Aqueous sorbent materials tested include solutions of sulfuric acid, nitric acid and phosphoric acid. The volatility and polarity of silicon compounds presented in biogas are strongly variable (see Table 2) [14]. Trimethylsilanol, which is found primarily in landfill gas as a degradation product of (dimethyl)siloxanes, is the most volatile silicon compound and in contrast to siloxanes, it exhibits good water solubility. Unfortunately, trimethylsilanol is not commercially available and therefore was not considered in our experiments. Absorption experiments were conducted with the most volatile linear siloxane, L2 and a cyclic siloxane of low volatility, D5, respectively.

The efficiency of hot concentrate sulfuric acid in eliminating gaseous siloxanes is already known [13]. Practical application of this absorbent, however, seems problematic due to its corrosive potential. Hence, solutions of H₂SO₄ differing in concentration and working temperature were tested to determine the mildest conditions for quantitative siloxane removal (Table 3). We found that the siloxanes studied were eliminated almost quantitatively using concentrated (97 wt.%) sulfuric acid at a temperature of 60°C. With sulfuric acid at room temperature, only 56–70% was removed for both L2 and D5. Quantitative siloxane removal was possible also with half-concentrated H₂SO₄ (48 wt.%) at 60°C. A further decrease to an acid concentration of 24 wt.% resulted in a significant decline in siloxane elimination efficiency, which was found to be 64–73%.

In recent years, the effect of ultrasound on the acid catalyzed ring opening polymerization of D4 was described [15]. Sonication led to enhanced reaction rates and yields, which was explained by the efficient mixing and dispersal of the acid catalyst. In order to evaluate the effect of ultrasound on the removal of gaseous siloxanes by sulfuric acid, the gas washing bottle filled with 50 ml of 97% H₂SO₄ was immersed in an ultrasonic bath (35 kHz, 230 W).

Table 3
Siloxane removal by gas–liquid extraction

Sorbent material	Remarks	Siloxane elimination efficiency	
		D5 (%)	L2 (%)
Sulfuric acid, 97%	Temperature, 60°C	>95	>95
Sulfuric acid, 48%	Temperature, 60°C	>95	>95
Sulfuric acid, 24%	Temperature, 60°C	68–73	64–70
Sulfuric acid, 97%	Temperature, 20°C	65–70	56–61
Sulfuric acid, 97%	Temperature, 20°C, ultrasound (35 kHz)	72–77	60–65
Nitric acid, 65%	Temperature, 60°C	>95	>95
Nitric acid, 65%	Temperature, 20°C	48–53	40–43
Nitric acid, 33%	Temperature, 60°C	70–75	70–75
Phosphoric acid, 85%	Temperature, 60°C	44–48	53–60

Only a poor effect was observed with an elimination rate of 60–77%. This may be explained by the short contact time of siloxane and absorption solution, whereas the experiments conducted by Price et al. [15] involved several hours of reaction time. A major drawback of using sulfuric acid is the fact that traces of H₂SO₄ may be stripped from the absorption column and enter the combustion engine, leading to increased corrosion. As an alternative, nitric acid was evaluated as a potential siloxane removing agent since even in concentrated form, it does not corrode iron vessels due to chemical passivation. We found that using hot concentrated nitric acid a quantitative siloxane elimination was possible. Again, elevated temperatures turned out to be necessary as the application of concentrated nitric acid at room temperature resulted in a siloxane reduction of only 40–53%. Furthermore, high acid concentrations are required since the application of 33% nitric acid at a temperature of 60°C led to siloxane elimination rates of 70–75%. Concentrated phosphoric acid was found to be quite ineffective in removing siloxanes as even at temperatures of 60°C, an elimination rate of only 44–48% for D5 and 53–60% for L2 was obtained.

3.2. Siloxane removal by solid phase adsorption

Adsorbent materials used in this study were two kinds of polymer beads (Tenax TA, 60/80 mesh; Amberlite XAD II, 20/60 mesh), two kinds of inorganic adsorbents (molecular sieve 13X, 45/60 mesh; silica gel, particle size 1–3 mm) and two adsorbents with carbon as the major component (activated charcoal, particle size 2.5 mm; Carbopack B, 60/80 mesh). Since biogases contain a broad range of different compound classes with concentrations covering several orders of magnitude, a competitive adsorption of siloxanes and a variety of trace compounds must be considered. Thus, large adsorption capacities for the target silicon compounds are essential for adsorbent materials used in gas pretreatment. In our experiments the adsorbents (0.5 g) were exposed to 5 mg siloxanes. Only those materials which did not show any breakthrough were considered useful for practical application. Adsorption experiments were conducted with the most volatile linear siloxane, L2 and a cyclic siloxane of low volatility, D5, respectively.

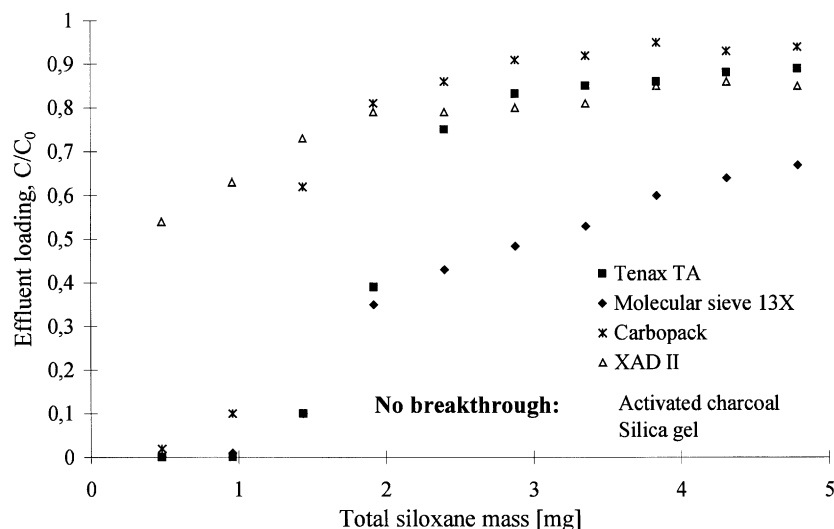


Fig. 2. Breakthrough curves of solid sorbent materials in experiments involving hexamethyldisiloxane (L2).

We found that all adsorbents tested exhibited large adsorption capacities for the siloxane D5. In the case of Tenax TA and molecular sieve 13X, a slight breakthrough at a siloxane uptake above 4.5 mg was observed with effluent loading between 18 and 7% of the initial siloxane concentration. All other adsorbents were exposed to 5 mg D5 without any breakthrough. The adsorption capacities of some adsorption materials were found to be markedly lower in experiments with the more volatile siloxane L2. Breakthrough curves for L2 experiments are indicated in Fig. 2. Then, the effluent loading (C/C_0) is plotted against the total mass of siloxane passed over the adsorbent bed. Amberlite XAD II was found to be especially unsuitable for L2 adsorption. After exposing the adsorbent material (0.5 g) to a total siloxane mass of 0.5 mg (200 ml/min, 1.2 g/m³, 2 min), the effluent contained 55% of the initial L2 concentration. Interestingly, Amberlite XAD II has already been used as adsorbent for the analysis of siloxanes in biogases [13]. For L2 on Carbopack B (graphitized carbon) a breakthrough threshold ($C/C_0 > 0.05$) of 0.5 mg was observed, and after exposing the material to a total siloxane mass of 3 mg, the adsorption capacity was near-saturated. The adsorbents (0.5 g) Tenax TA and molecular sieve 13X showed similar thresholds of 1 mg. However, the adsorption capacity of molecular sieve turned out to be substantially higher than that of Tenax, since its breakthrough curve was distinctly flatter and even after exposing the material to 5 mg L2 the effluent siloxane content was only 70% of the initial test gas concentration. Complete L2 elimination was achieved using activated charcoal and silica gel, respectively. In both cases, at a siloxane uptake of 5 mg the effluent loading C/C_0 was <0.05 .

According to these experiments silica gel seemed to be an especially promising and highly cost-effective candidate for an application in gas pretreatment, since this can be used simultaneously for biogas drying. Thus, additional experiments with silica gel with

regard to thermal regenerability were conducted and the adsorption capacity for siloxanes was studied at different moisture contents. Finally, the suitability of silica gel as siloxane removing agent was evaluated at a sewage treatment plant.

3.2.1. Thermal regeneration

For thermal desorption studies the silica gel was loaded with 10 mg/g siloxane (L2 and D5, respectively). The adsorption tube was turned upside down, wrapped in resistance wire and heated to 250°C for 20 min. The carrier flow rate applied was 200 ml/min. Again, the siloxanes were absorbed in organic solvent and quantified by GC/FID. For both the siloxanes L2 and D5 an excellent desorption efficiency greater than 95% was observed. In similar studies using activated charcoal as adsorption material the thermal regeneration was less effective. While desorption of the volatile hexamethyldisiloxane L2 was possible at efficiencies greater 95%, only 74–83% of the siloxane D5 were desorbed from activated charcoal under the given conditions. Due to the fact that siloxanes of low volatility (D4, D5, D6) constitute the majority of silicon compounds present in sewage gas and landfill gas, a continuous loss of activity from one application to the other will happen if activated charcoal is used in gas pretreatment for siloxane removal.

3.2.2. Adsorption of siloxanes in moist gases

Due to the high adsorption capacity of silica gel for siloxanes, these experiments were conducted at increased test gas concentrations of 4 g/m³ L2 and D5, respectively. To obtain test gases of different humidity, nitrogen was bubbled through a gas washing bottle filled with water and diluted with dry nitrogen. The moisture content was determined using a humidity sensor (type FH A646, Ahlborn, Holzkirchen/Germany). This moist gas flow was split to give flows 1 and 2 (Fig. 1). Prior to loading with siloxane, the silica gel (0.5 g) was equilibrated using nitrogen of the given humidity until the effluent reached inlet moisture level. The water uptake of the silica gel at each humidity as well as the siloxane uptake at saturation (effluent loading $C/C_0 > 0.9$) were determined gravimetrically.

Breakthrough curves obtained in experiments with D5 are shown in Fig. 3. Again, the effluent loading (C/C_0) is plotted against the total mass of siloxane passed over the adsorbent bed. Further results including experiments with the siloxane L2 are given in Table 4. Using dry nitrogen as a carrier gas, the threshold siloxane mass was determined to be 59 (L2) and 52 mg (D5). The higher adsorption capacity for the polar hexamethyldisiloxane is not surprising since silica gel is hydrophilic in nature. Experiments were conducted at 10, 20, 30 and 50% relative humidity (RH). Note, that at 10% RH only a slight decrease of the siloxane uptake for both the siloxanes L2 and D5 was observed. The breakthrough thresholds of L2 and D5 were determined to be 52 and 44 mg, respectively. As expected, with increasing moisture content the adsorption capacity for siloxanes decreased significantly. At a relative humidity of 30%, the siloxane uptake at saturation was 45 (L2) and 41% (D5) of the uptake in experiments using dry nitrogen as carrier gas. Parallel to the decreased adsorption capacity, the breakthrough curves became distinctly flatter with increasing moisture level. Thus, at a RH of 50% the siloxane uptake at breakthrough ($C/C_0 > 0.05$) was <3 mg in D5 experiments. The maximum siloxane uptake at RH 50% was determined to 19 (L2) and 14 mg (D5).

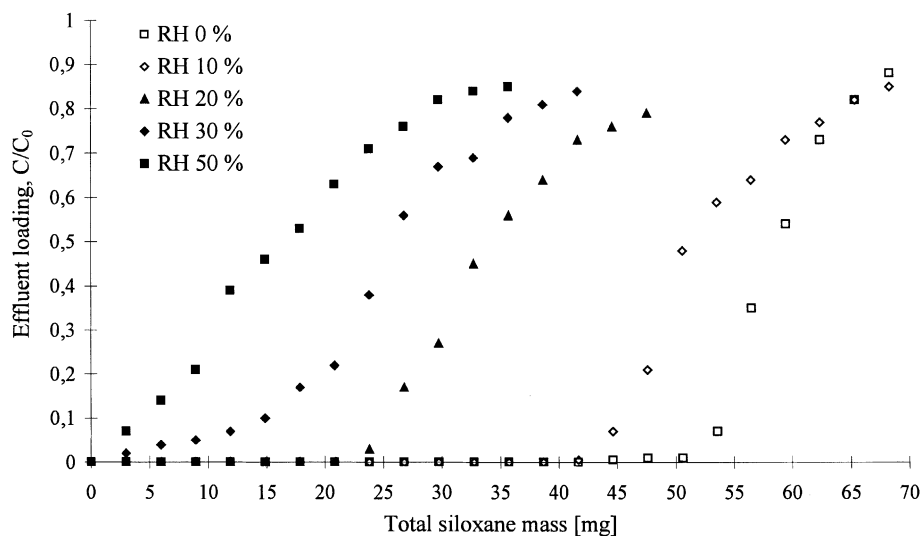


Fig. 3. Breakthrough curves of silica gel in experiments involving D5 at different gas moistures.

3.2.3. Siloxane removal in sewage gas

In these studies, sewage gas was drawn through an adsorption tube (200 mm × 12 mm i.d.) filled with 2.0 g of silica gel at a flow rate of 1.0 l/min. The effluent was sampled into stainless steel canisters and analyzed according to [11]. Studies were conducted using both moist biogas ($RH_{20^{\circ}\text{C}} > 85\%$) and biogas dried by refrigeration ($RH_{20^{\circ}\text{C}} = 38\%$) (Fig. 4). The siloxane concentrations in the biogases were determined to be 16.2 and 14.8 mg/m³, respectively (see Table 5). As expected, the siloxane removing efficiency was highly dependent on the moisture content. In the case of raw sewage gas, even at a contact volume of 50 l/g more than 60% of the siloxanes were found in the effluent and at 150 l/g the adsorption capacity of silica gel was nearly exhausted. Using dried biogas the adsorption capacity of silica gel for siloxanes was distinctly higher despite the fact that again a breakthrough (7%)

Table 4
Adsorption experiments at different gas moistures using 0.5 g silica gel

Relative humidity (20°C) (%)	Water uptake (mg)	Siloxane uptake at saturation ($C/C_0 \approx 1$) (mg)		Siloxane uptake at breakthrough ($C/C_0 = 0.05$) (mg)	
		L2	D5	L2	D5
		0	0	64–67	54–59
10	18–20	54–57	47–50	50–54	42–45
20	32–36	40–43	33–36	31–35	23–27
30	43–47	28–30	22–24	9–11	5–6
50	55–58	21–23	15–17	4–5	<3

Table 5
Effects of gas pretreatment installations on the siloxane concentration

Site studied	Waste disposal site	Sewage treatment plant A			Sewage treatment plant B
Gas pretreatment installation	Refrigeration condenser	Refrigeration condenser	Adsorption bed (silica gel)	Adsorption bed (meadow ore)	Adsorption bed (meadow ore)
Installation purpose	Biogas drying	Biogas drying	Biogas drying	H ₂ S removal	H ₂ S removal
Siloxane concentration in biogas before treatment (mg/m ³)	Trimethylsilanol 2.8–3.2				
	L2 0.7–0.9	L2 < 0.05	L2 < 0.05	L2 0.06–0.08	L2 < 0.05
	D3 0.40–0.44	D3 0.24–0.25	D3 0.24–0.25	D3 0.35–0.42	D3 0.32–0.35
	D4 4.8–5.1	D4 6.3–6.6	D4 6.3–6.6	D4 7.7–8.2	D4 7.5–7.7
	D5 0.60–0.65	D5 9.4–9.9	D5 9.4–9.9	D5 14.8–15.5	D5 11.3–12.0
Siloxane concentration in treated biogas (mg/m ³)	Trimethylsilanol 2.2				
	L2 0.7–0.8	L2 < 0.05	L2 < 0.05	L2 < 0.05	L2 < 0.05
	D3 0.35–0.42	D3 0.15–0.19	D3 < 0.05	D3 0.24–0.25	D3 0.15–0.18
	D4 4.5–4.6	D4 6.0–6.2	D4 0.05–0.07	D4 6.3–6.6	D4 2.1–2.2
	D5 0.50–0.53	D5 8.2–8.7	D5 0.20–0.22	D5 9.4–9.9	D5 2.6–2.8
Siloxane removal (%)	11	9	>98	31	75

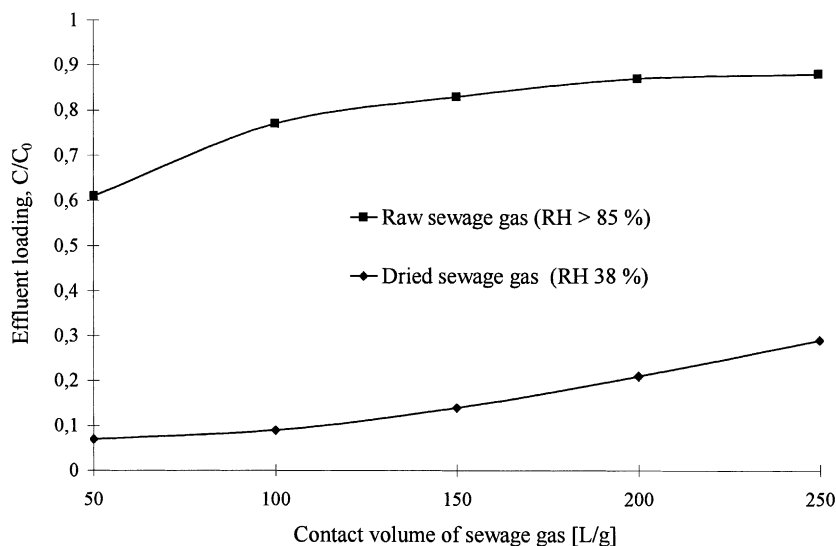


Fig. 4. Breakthrough curves of silica gel using raw sewage gas (RH > 85%) and dried sewage gas (RH 38%).

at a contact volume of 50 l/g was observed. The breakthrough profile, however, turned out to be extremely flat, and as a consequence at a contact volume of 250 l/g only 29% of the initial present siloxanes were found in the effluent of the silica gel adsorption tube.

3.3. Evaluation of gas pretreatment installations for their siloxane removing efficiency

3.3.1. Biogas drying by refrigeration condensers

In order to evaluate the effect of biogas refrigeration on the reduction of siloxane content, raw gas and dried gas originating from both a waste disposal site and a sewage treatment plant was sampled and analyzed according to [11]. At both sites studied, the biogas was dried to a dew point of 5°C, corresponding to a relative humidity of 38% at 20°C. We found that the biogas refrigeration had some effects on the concentration of low volatile organic trace compounds which were reduced by 20–25%. Among silicon compounds, the content of the low volatile siloxane D5 was slightly reduced to 82–88% of the initial concentration (Table 5). The effect of gas refrigeration on the concentration of trimethylsilanol found in landfill gas was more marked. Due to its water solubility it was washed out by the formed condensate and reduced by 27%. However, in both the dried landfill gas and sewage gas more than 88% of the initial siloxane concentrations were still present.

3.3.2. H₂S removal by meadow ore

At both sewage treatment plants studied adsorbent beds with meadow ore (consisting primarily of iron oxides like lepidokrite and goethite) for the removal of H₂S were installed. The elimination of hydrogen sulfide is obtained according to $2\text{Fe}(\text{OH})_3 + 3\text{H}_2\text{S} \rightarrow 2\text{FeS} + \text{S} + 6\text{H}_2\text{O}$. The loaded adsorbent material is easily regenerated by hot air ($2\text{FeS} + 3/2\text{O}_2 \rightarrow$

$2\text{Fe}(\text{OH})_3 + 2\text{S}$). At both sites a significant effect on the silicon content in the biogas was observed. In the case of sewage treatment plant A, 31% of the siloxanes were eliminated and in case of site B even a silicon reduction by 75% was obtained. The elimination rates were similar for all the siloxanes found in sewage gas (D3, D4, D5). The siloxane removing potential of meadow ore may be explained by ‘active sites’ which catalyze oligomerization and hydrolysis reactions. Lehmann et al. [16] and in earlier studies by Buch and Ingebrigtsen [17] described the degradation of siloxanes on a variety of soil surfaces to give water soluble silanols. In these studies, they found a distinct dependence of the siloxane degradation rate and the soil moisture. Thus, differences in the meadow ore as well as a varying moisture content in the adsorbent beds may explain the different siloxane elimination efficiencies at the sites studied.

3.3.3. Adsorptive gas drying

At the sewage treatment plant A an adsorption bed for biogas drying has been installed in addition to the refrigeration condenser. This bed is used during interruptions of the gas combustion and electricity generating systems. In such cases, the sewage gas is fed into a buffering gas tank and pressurized up to 5 bar. Parallel to pressurization the biogas is dried over silica gel to a dew point of -50°C . We found that this gas pretreatment installation combined with gas drying achieved a quantitative elimination of siloxanes. In Fig. 5, element specific chromatograms of raw sewage gas and sewage gas treated by adsorptive drying are shown together with a list of the major trace compounds identified by GC/MS analysis.

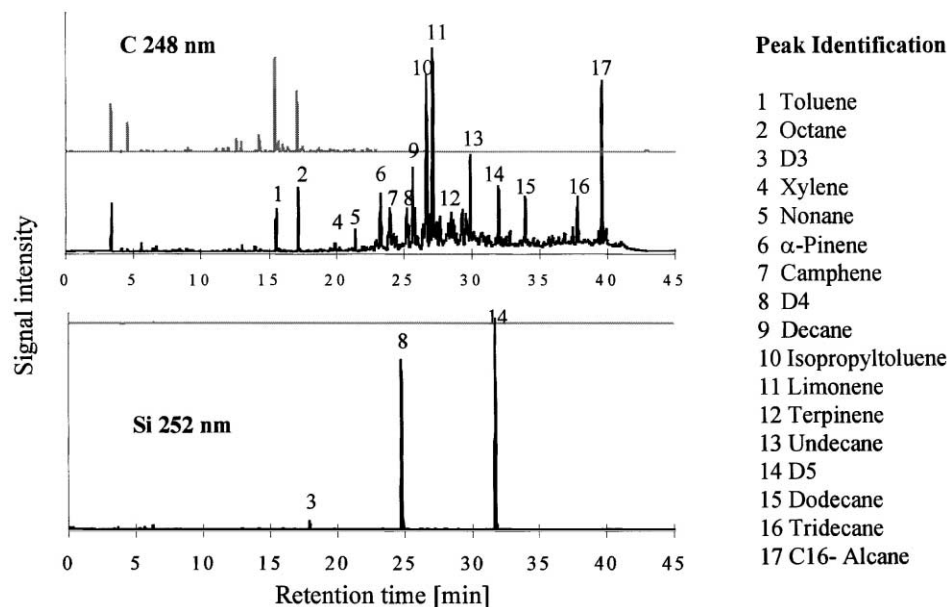


Fig. 5. Element specific chromatograms of sewage gas before adsorptive drying (black color) and after drying with silica gel (grey color).

The elimination efficiency for all siloxanes (D3, D4, D5) was determined to be greater than 98%. Parallel to the siloxanes, organic trace compounds with boiling points higher than 130°C were also removed almost quantitatively. The combustion engine was fed by relatively pure biogas since a variety of halides (i.e. chlorobenzenes) were also removed. The regeneration of silica gel was obtained by hot air, which was conveyed counter-currently into the previously depressurized adsorbent bed. Up to now, the loaded regeneration gas was added to the exhaust. In order to avoid the emission of VOCs adsorbed on silica gel, however, a separate combustion of the regeneration gas is highly recommended.

4. Conclusions

In laboratory studies, the use of half-concentrated sulfuric acid at a temperature of 60°C produced quantitative siloxane removal. Similar elimination rates were obtained using concentrated nitric acid, which may be an alternative to sulfuric acid due to its noncorrosive properties. Although the efficiency of these materials is high, a practical application as adsorbent media for biogas pretreatment should be performed very carefully because of their high potential risk for health and environment.

According to results obtained in laboratory studies and in experiments at sewage treatment plants, silica gel may be used effectively in gas pretreatment to reduce the silicon content since it showed adsorption capacities for siloxanes of more than 100 mg/g. A prerequisite for its application is preliminary gas drying which may be achieved by a further silica gel bed. More elegant is the use of silica gel beds working at elevated pressure since both a very effective biogas drying and a quantitative siloxane removal is achieved. The material can be easily and cost-effectively regenerated. In cases where hydrogen sulfide has to be removed from biogas prior to its utilization as a fuel for electricity generation (which is true especially for sewage treatment plants), the application of meadow ore may result in a significant reduction of the siloxane content. In contrast to this, no siloxane reduction is achieved by biogas refrigeration as the sole gas treatment.

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