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Biological Removal of Siloxanes from Landfill and Digester Gases: Opportunities and Challenges

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The presence of volatile methyl siloxanes (VMSs) presents challenges for using landfill and digester gases as energy fuels because of the formation of silicon dioxide deposits during combustion. This study looks at the feasibility of using biological treatment to control VMSs. Biotrickling filters removing octamethylcyclotetrasiloxane (D4), selected as a model VMS, from aerobic and anaerobic waste gas streams were setup. The efficacy of both aerobic and anaerobic biotrickling filters was low. The removal of D4 in the aerobic biotrickling filter followed a linear trend, reaching 43% at a gas empty bed residence time of 19.5 min. Aerobic biodegradation of D4 in shake flasks was found to be extremely slow, with trace concentrations requiring 3−4 months for complete degradation. Gas−liquid partition tests revealed that D4 partitions poorly into aqueous phases and that interphase mass transfer is slow. Using the mass transfer data, we estimated the maximum possible mass transfer rate of D4 in the biotrickling filter to be in the range of 30−100 mg m^{-3} h^{-1}. These values are low and suggest that mass transfer limitations play an important role in the low treatment performance that was observed. The possibility of enhancing D4 mass transfer by using oleyl alcohol as a second nonmiscible liquid phase was unsuccessful. Overall, the results demonstrate that biological treatment of D4 vapors is possible but poses significant challenges.

Introduction

Polydimethylsiloxanes (PDMS) are a class of organosilicon compounds widely used in several industrial and household applications. These PDMS hydrolyze to lower-molecular-weight volatile methyl siloxanes (VMSs) and subsequently volatilize from waste at landfills and wastewater treatment plants (*1*). As a result, biogas produced at such facilities often contains trace amounts of VMSs (*2*−*4*), which form silicon dioxide deposits on the surfaces of equipment when combusted for energy generation. Over time, this silicon dioxide can accumulate to layers of up to several millimeters thick (*4, 5*). This causes a decrease in the efficiency of the equipment, as well as an increase in maintenance costs (*6, 7*). The presence of VMSs in biogas is thus a challenge for its effective use in boilers, electrical generators, and fuel cells.

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The amount of VMSs found in landfill and digester gases varies according to the source. Concentrations of up to 140 mg m^{-3} have been reported in both landfill and digester gases (*2*). This is significantly above the 15 mg m^{-3} limit recommended by most equipment manufacturers for unhindered use (*6*). Of all VMSs in biogas, octamethylcyclotetrasiloxane (D4) is the most abundant, with reported concentrations of up to 60% of total VMSs in landfill gas (*8*). It is thus imperative to develop economical and effective VMS treatment technologies for biogas to increase the feasibility of using biogas as an energy fuel.

It is only recently that engineers have been concerned with the development of methods to control VMSs from landfill and digester gases. So far, current technologies for VMSs control are only moderately effective. They include adsorption onto activated carbon beds, chilling and condensation, and absorption into solvents (*6, 9*), which are costly because of the added expenses of pretreatment, or the costs of regeneration or disposal of used media (*10*). Biological techniques to remove pollutants from gaseous phases are attractive alternative technologies that are often economical and environmentally friendly (*11*).

Amidst little research that has been done on biodegradation of siloxanes, there have been some promising results. PDMS compounds have been found to be biodegraded in soils (*12, 13*). The speculated pathway for this is believed to be chemical decomposition of PDMS to VMSs and dimethylsilanediol (DMSD) first, and then aerobic biological degradation of DMSD to benign compounds (*13, 14*). Sabourin et al. (*13*), however, observed that the rate of biodegradation of DMSD was very slow at 2−4% decomposition per month. Grümping et al. (*15*) found that 3% D4 was mineralized anaerobically to DMSD by a mixed culture obtained from a sewage treatment plant after 100 days of incubation. DMSD was then consumed to form the final end-products, which were not identified.

Hence, the objective of this study was to determine whether removal of VMSs from biogas could be carried out in gas-phase bioreactors, either aerobically or anaerobically. D4 was selected as a model VMS. First, mixed cultures potentially degrading D4 as sole carbon and energy source were enriched, and used to inoculate a biotrickling filter that was fed with synthetic gas containing D4 in air. Biogas usually contains little or no oxygen, and thus direct anaerobic treatment to remove D4 was also investigated in a biotrickling filter fed with oxygen-free synthetic gas. To better understand the effects of D4 hydrophobicity on the treatment process, gas−liquid partition tests were carried out. Finally, the possibility of adding a nonaqueous liquid phase to the bioreactors to enhance the mass transfer of D4 was evaluated.

Materials and Methods

Enrichment Cultures. Cultures degrading D4 were enriched in a mineral medium comprising 1 g L^{-1} KH_2PO_4, 1 g L^{-1} K_2HPO_4, 1 g L^{-1} KNO_3, 1 g L^{-1} NaCl, 0.2 g L^{-1} $MgSO_4$, 0.026 g L^{-1} $CaCl_2 \cdot 2H_2O$ (*16*), 2 mL L^{-1} solution of trace elements (*17*), and 0.2 mL L^{-1} of a solution of peat humic substances (Biogene, Prodex, Acron, OH) (*18*), and transferred regularly. Two-hundred-fifty milliliter flasks were filled to 100 mL with mineral medium and initially inoculated with activated sludge from the City of Riverside Wastewater Treatment Plant (Riverside, CA). The medium was supplemented with 500 mg L^{-1} D4 (purum, Sigma-Aldrich Corp., St. Louis, MO), which is well above its reported water solubility of 0.056 mg L^{-1} (*1*). D4 was the only carbon and energy source provided to the cultures. The cultures were stirred on a rotary shaker at 120

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rpm and aerated monthly. Anaerobic cultures were prepared the same way, except for sparging gas headspace with nitrogen and adding 1 g L^{-1} of Na_2CO_3 in the mineral medium. Microbial growth in all flasks was monitored through regular optical density (OD_{600}) measurements.

Biotrickling Filter Setups. A schematic of the experimental setup is shown in Figure S1 (see the Supporting Information). Synthetic gas containing D4, to be treated in the aerobic biotrickling filter, was produced by sparging compressed air through a 1 L bottle containing water at room temperature, and then passing the humid air through a 250 mL bottle containing an open-top 40 mL vial filled with D4. The air flow rate was maintained at 0.5 L min^{-1}. This setup resulted in concentrations of D4 of 45 ± 5 mg m^{-3} in the gas phase, which is in the same range as concentrations seen in practice. The D4-laden gas stream was then split into two, with one stream going to the biotrickling filter entering from the bottom, and the other to a vent, thus allowing regulating the flowrate without changing the inlet concentration of D4. The anaerobic biotrickling filter was run the same way, except that nitrogen was used instead of compressed air.

The biotrickling filters were constructed from a clear PVC pipe (Harrington Plastics, Chino, CA) 45 cm long and 3.8 cm in internal diameter. The packing material was 360 g of cattle bone Porcelite (CBP, Aisin Takaoka Co. Ltd., Japan), a quasi spherical porous ceramic of 3 mm average particle diameter with incorporated slow-release nutrients (*19*). The active bed height was 34 cm, the bed volume was 390 cc, and the bed void volume was 42%.

For the anaerobic biotrickling filter, lava rocks of 10 mm average particle diameter were used as the packing material. The active bed height and volume were the same as the aerobic biotrickling filter; however, the void volume was 58%.

The biotrickling filters were inoculated initially with 50 mL of enriched D4-degrading culture and 50 mL of fresh activated sludge, and then every two months with 30 mL of enriched D4-degrading culture. Mineral medium was continuously recirculated over the bed at a rate of 0.185 m h^{-1} using a peristaltic pump. A constant hold-up of 80 mL of liquid was maintained at the bottom of the biotrickling filters. Every 3 days, 50 mL of the liquid was drained and replaced by fresh mineral medium. Water was added periodically to compensate for evaporative losses. The pH of the recirculating liquid in the biotrickling filters was between 7 and 7.5. The pressure drop across the beds of both the bioreactors remained under 5 cm of water gauge.

The aerobic biotrickling filter was operated continuously for a total of 12 months, whereas the anaerobic biotrickling filter was operated for 6 months.

Partition Tests. Partition tests for D4 between gas and liquid phases (deionized water, mineral medium, cell suspension, and oleyl alcohol) were carried out. 250 mL flasks were filled with 125 mL of the liquid of interest, and gas phase D4 was injected into the headspace to obtain concentrations of 50 ± 5 mg m^{-3}. The flasks were allowed to equilibrate by placing them on a rotary shaker at 100 rpm for different amounts of time, to observe the effect of time on the partition of D4. All tests were conducted at 26 °C. Concentrations of D4 in the headspace were then measured for each flask, on the basis of which concentrations in the liquid phase and the gas−liquid partition coefficients were calculated. Replicate flasks were analyzed for each condition.

The cell suspension for partition tests was from a toluene-degrading mixed culture grown in a bubble column in the laboratory (1−2 g m^{-3} toluene in air, same mineral medium as for D4 cultures, OD_{600} = 0.25). Controls made using autoclaved samples showed that no biodegradation of D4 occurred within the time span of the partition tests.

The time-dependent dimensionless partition coefficient of D4 was calculated using the following equation.

$$P = \frac{C_G^*}{C_L^*} \quad (1)$$

where C_G^* = time-dependent gas phase concentration of D4 (mg m^{-3}), and C_L^* = time-dependent liquid phase concentration of D4 (mg m^{-3}).

Experiments with Two-Liquid-Phase Bioreactor Systems. In order to possibly improve the mass transfer of D4, a second liquid phase with good partitioning for D4 was used in some experiments. Oleyl alcohol (60%, Sigma-Aldrich Corp., St. Louis, MO), which is nonmiscible with water, was selected on the basis of earlier studies with toluene vapors (*20*).

An aerobic two-liquid-phases biotrickling filter, with a similar configuration as described above and inoculated with enriched cultures and activated sludge, was setup. Instead of mineral medium only, a 20:80 (vol) emulsion of oleyl alcohol and mineral medium was recirculated through the bed. The reservoir for the liquid was outside the reactor, which allowed for effective mixing of the emulsion. This biotrickling filter was operated for 3 months.

Gas Analysis. Concentrations of D4 in gas phase were measured on an HP 5890 Series II gas chromatograph (Hewlett-Packard, Wilmington, DE) fitted with a 30 m × 0.32 mm × 0.25 μm HP-5 column operated from 50 °C (2 min isothermal) to 120 °C (1 min isothermal) at 15 °C min^{-1}. The carrier gas was helium and the detection was with a flame ionization detector. A 5 mL injection loop was used for injecting gas samples onto the column. The retention time of D4 under these conditions was 4.9 min, and the detection limit was 1 mg m^{-3}. The method allowed for rapid quantification of D4 in the synthetic waste gas but it may not be adequate for digester or landfill gases, which contain a variety of VMSs and other compounds.

CO_2 concentrations in the aerobic biotrickling filter inlet and outlet were determined using an infrared sensor and a data logger (Vernier Instruments, Beaverton, OR).

Results and Discussion

Batch Biodegradation of D4. Cultures enriched aerobically and anaerobically with D4 as the only carbon and energy source showed an increase of only up to 0.05 OD_{600} units over nine months. This slow biomass growth is believed be the result of the poor availability of D4 to the cultures because of its high partition coefficient and low water solubility as well as possibly the low biodegradability of D4. Eight months after the first cultures were prepared and then subsequently transferred, selected flasks incubated aerobically were supplemented with D4 only in the gas phase (50 ± 5 mg m^{-3}) and monitored for D4 biodegradation via headspace analysis. It took three to four months for all the D4 to be consumed. Controls prepared using autoclaved cultures showed little or no (<10%) decrease in D4 concentrations over the same amount of time. Grümping et al. (*15*) observed only a 3% degradation of D4 after 100 days incubation, although this was for anaerobic cultures. The complete decomposition observed here in a similar time may be due to the fact that aerobic biodegradation could be faster and/or that the cultures had already been enriched with D4 for eight months, and thus the microorganisms had adapted to using D4 as a substrate. Similarly, very low activity was observed in shake flasks incubated anaerobically. In both aerobic and anaerobic cases, the increase in OD_{600} was not significant. This indicates the absence of measurable cell growth, and thus no growth kinetics parameters could be calculated.

Despite the slow growth of the cultures on D4 as the sole carbon source and the extremely slow batch biodegradation

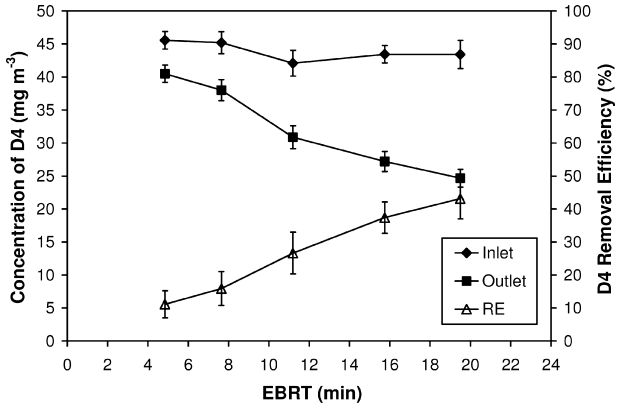

FIGURE 1. Effect of EBRT on the performance of the aerobic biotrickling filter. Errors bars are the standard errors.

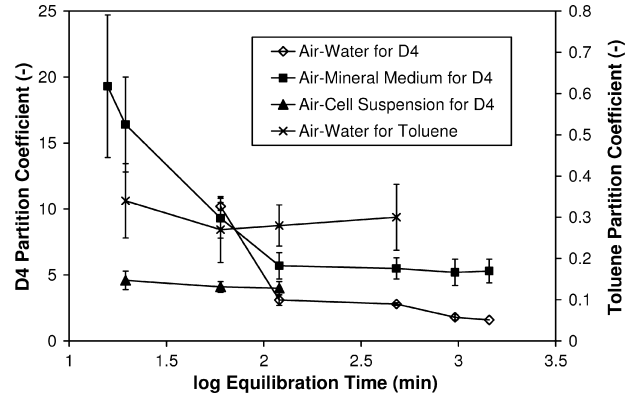

FIGURE 2. Effect of equilibration time on the dimensionless partition coefficient of D4 between gas and liquid phases. Errors bars are the standard errors.

of D4, it was anticipated that bioreactors inoculated with the enrichment cultures could perform better than expected from D4 removal data in shake flasks, because of the higher cell density that can be achieved in an immobilized cell bioreactor. Several compounds that have been shown to be poorly degraded in batch cultures have been successfully removed in bioreactors. One of the prime examples of such compounds is methyl *tert*-butyl ether (MTBE). A much faster MTBE biodegradation rate was obtained in a biotrickling filter compared to batch studies (*21*). The biotrickling filter exhibited an unprecedented performance in terms of removal of MTBE under a variety of conditions (*18, 22*).

Other examples of poorly degraded compounds successfully removed in bioreactors include nitriles such as pyridine, and nitroaromatics such as nitrobenzene. Pandey et al. (*23*) studied the biodegradation potential of pyridine before running a biofilter degrading pyridine and found it to be extremely slow. Nonetheless, the biofilter showed removal of pyridine up to 99% even at high mass loadings. Efficient removal of nitrobenzene, with an elimination capacity as high as 50 g m^{-3} h^{-1}, has been observed in a biotrickling filter, even though the growth in batch cultures was very slow (*24*). Thus, it was believed that despite the slow growth of suspended microorganisms on D4, the removal in a bioreactor by immobilized microorganisms would be much better.

Aerobic Biotrickling Filter Performance. The performance of the aerobic biotrickling filter was monitored over eight months at empty bed residence times (EBRTs) of 50−120 s. Under these conditions, up to 10% removal of D4 was observed, a value that is inconclusive because the error range of the analysis was about 5−6%. This suggests that the microbial consortium used for inoculation of the system had not acclimatized and reached a sufficient cell density in the bioreactor and/or that D4 was mostly unavailable due to mass transfer limitation. The removal efficiency (RE) observed in this study is comparable to that of 10−20% reported very recently by Accettola et al. (*10*) for a biotrickling filter removing D3 at an EBRT of 3.5 min. D3 is another VMS found in biogas, but it is less hydrophobic than D4.

Subsequently, the EBRT was increased significantly, the reactor was reinoculated with fresh enriched cultures, and the performance analyzed a month later. A larger EBRT means a longer contact time for D4 to transfer to the biofilm and be degraded, however it also means that a larger bioreactor will be required for practical applications. Nonetheless, it was important to know at what EBRT significant biodegradation of D4 takes place. The biotrickling filter exhibited a linear increase in D4 removal with an increasing EBRT (Figure 1) reaching 43% removal at an EBRT of 19.5 min. At even greater EBRTs, the RE seemed to deviate from the linear trend with only a 50−60% removal observed at 30−40 min (data not shown). At an EBRT of 4.5 min, a consistent removal of just over 10% was observed. Overall, this is a significant improvement over the rate of D4 biodegradation in shake flasks, probably due to greater cell density and surface area for mass transfer. Still, the very long EBRTs required for even marginal D4 removal suggest that significant improvements are needed for practical application.

To confirm that the observed removal of D4 in the biotrickling filter was due to biodegradation, CO_2, the expected byproduct of the aerobic biodegradation of D4 was determined in the effluent of the biotrickling filter at an EBRT of 19.5 min. The CO_2 production with and without D4 in the inlet was determined. It was found that all eight carbons in D4 were stoichiometrically converted CO_2. The stoichiometric conversion to CO_2 is consistent with the quasi-absence of visible growth observed in shake flasks and in the biotrickling filters over time. Even so, this is the first reported proof of the aerobic biodegradation and mineralization of D4.

Anaerobic Biotrickling Filter Performance. The anaerobic biotrickling filter was operated for six months at an EBRT of 4 min. The longer EBRT was motivated by the modest removal obtained with the aerobic bioreactor. The maximum D4 removal observed was 15%, i.e., relatively similar to the performance observed with the aerobic biotrickling filter. In the absence of oxygen, the microorganisms could potentially use nitrate or sulfate as an electron acceptor. However, a change in the electron acceptor did not significantly affect the performance of the bioreactor (results not shown). In light of the low D4 removal, nitrate and sulfate reduction was not monitored, and the anaerobic biotrickling filter was not tested at higher EBRTs.

Gas−Liquid Partition of D4. One of the most important parameters governing the mass transfer of a pollutant from the gas phase into the aqueous phase where it is biodegraded is its Henry's constant. There are inconsistent reports of Henry's law coefficient for D4 in the literature, with dimensionless values between 1.5 and 32 reported by different researchers (*25−29*). Additionally, the theoretically predicted Henry's constant for D4 using EPISuite software is 3.57 (*30*). Because of these discrepancies, the partition of D4 between air and various aqueous phases (water, mineral medium, cell suspension) was investigated.

For gas−liquid equilibration times of 1 h, the partition coefficient for D4 between air and water was 10.2 ± 0.8, and that between air and mineral medium was 9.3 ± 1.5. However, it was found that gas−liquid equilibrium was not achieved within 1 h, as tests with longer equilibration times saw a decrease in the partition coefficient (Figure 2, and Table S1 in the Supporting Information). In general, compounds with a high molecular weight exhibit a higher resistance to mass transfer in the liquid film (*28*) which could be one of the reasons why it took over 2 h for D4 to reach gas−liquid

equilibrium. To confirm that the longer equilibration time for D4 was due to its physicochemical properties and not related to the experimental protocol, we also carried out tests with toluene vapors. Analysis for four different equilibration times ranging from 0.32 to 4 h demonstrated that toluene partitioned into water much faster than D4.

Figure 2 shows the time-dependent partition coefficients of D4 plotted against logarithm of the equilibration time for each of the different liquids. Although D4 vapors partitioned faster into mineral medium (2 h) compared to into water (16 h), the air-mineral medium partition coefficient was three times higher. This is consistent with the fact that higher molecular weight compounds partition poorly into solutions that contain cosolutes and thus have a higher ionic strength than water. The mineral medium used for this study had an ionic strength of 60 mM. The equilibrium partition coefficient of D4 in mineral medium was found in the present study to be 5.7 ± 1.0, whereas that in water was 1.8 ± 0.1. Hamelink et al. (*28*) obtained the value 10.5 ± 7.2 for the partition coefficient of D4 between air and a seawater solution, which had a much higher ionic strength than mineral medium. Evidently, the presence of cosolutes in water and greater ionic strength increased the gas−liquid partition coefficient of D4.

Since the partition of D4 into mineral medium was found to be poor, it was hypothesized that increasing the mineral medium recirculation rate in the biotrickling filters, thereby increasing the wetting of the biofilm and the liquid hold-up, would result in additional mass transfer resistance, and thus lower treatment performance. To confirm this, the mineral medium recirculation rate in the aerobic biotrickling filter was doubled at an EBRT of 19.5 min. The RE of D4 dropped from 43 to 26%, confirming that severe mass transfer limitations occurred in the bioreactor.

These results also triggered determination of the partition of D4 between the gas phase and a cell suspension to determine the effect of the presence of microorganisms on gas−liquid equilibrium. Others had previously shown that hydrophobic compounds partition better into biofilm than into water, resulting in much better removal in gas-phase bioreactors than expected (*31*). However, partition of D4 into a cell suspension was found to be much poorer than into water, and only marginally better than into mineral medium. The equilibrium was, however, achieved faster (Figure 2).

Overall, the results from the partition experiments suggest that at the EBRTs tested in the aerobic biotrickling filter, equilibrium of D4 between gas phase and recirculating mineral medium phase was never achieved, and thus the availability to the microorganisms was governed not by the equilibrium of D4 between the two phases, but the time-dependent partition coefficient and mass transfer. In order to illustrate the effect of the partition time on the performance of the reactor, the RE of D4 in the biotrickling filter was plotted vs the time-dependent partition coefficient for times equivalent to the EBRTs tested in the reactor (Figure 3). At low EBRTs or low equilibration times, the partition of D4 into mineral medium was poorer, and thus corresponded to high partition coefficients and low removal of D4 in the reactor. At larger EBRTs or equilibration times, the partition of D4 into mineral medium was more favorable, and was associated with better reactor performances. There was, however, no simple relation between the two, suggesting that at higher EBRTs, the removal was governed not just by the partition and mass transfer, but the biology as well.

Maximum Mass Transfer Rate in the Biotrickling Filter. The results above indicate that mass transfer plays a significant role in limiting the removal of D4 in the biotrickling filters. The extent of mass transfer limitation in the biotrickling filters was estimated. First, the liquid film mass transfer coefficient of D4, k_L (m h^{-1}), was calculated by fitting the experimental data from the partition tests in shake flasks to eq 2.

$$V_G \frac{dC_G}{dt} = -k_L A\left(\frac{C_G}{P} - C_L\right) \quad (2)$$

where A is the interfacial area for mass transfer in the flasks during the partition tests. Because the flask was gently shaken horizontally, A could be estimated from the geometry of the flask and ranged from a low value of 0.007 m^2 up to 0.013 m^2, if considering maximum possible wetted area due to shaking. A good agreement between experimental and fitted data was observed ($R^2 = 0.91$, data not shown). The liquid film mass transfer coefficient obtained was between 2.1×10^{-3} m h^{-1} and 3.9×10^{-3} m h^{-1} depending on which value was used for A.

The maximum rate of D4 mass transfer ($\widehat{m}_{D4}$, mg m^{-3} h^{-1}) per unit volume of the aerobic biotrickling filter was calculated next using eq 3.

$$\widehat{m}_{D4} = k_L a_{btf}\left(\frac{C_G}{P} - C_L\right) \quad (3)$$

To apply eq 3, two assumptions were made. First the concentration of D4 in the liquid phase C_L was taken as being zero; this assumes that D4 biodegradation is faster than mass transfer. Second, C_G was taken as being either the inlet D4 concentration, or the log mean of the observed inlet and outlet concentrations. The values at an EBRT of 19.5 min were used (inlet 43.4 mg m^{-3}, outlet 24.7 mg m^{-3}).

The specific area a_{btf} in the biotrickling filter was estimated from eq 4 which applies to spherical packings (*32*). The uncertainty on a_{btf} due to nonideal packing and bed geometry was estimated to be ±20%; thus the specific area used in eq 3 ranged from 1860 to 2780 m^2 m^{-3}.

$$a_{btf} = \frac{6(1-\varepsilon)}{D_p} \quad (4)$$

Depending on the biotrickling filter interfacial area and the concentration of D4 (inlet or inlet/outlet log mean), the calculated values for the maximum rate of D4 mass transfer ranged from 29 to 55 mg m^{-3} h^{-1} for the largest flask area A, and from 53 to 98 mg m^{-3} h^{-1} for calculations made with the lowest estimate for the flask area. These values should be compared to the loading and elimination of D4, which at an EBRT of 19.5 min were 151 mg m^{-3} h^{-1} and 63 mg m^{-3} h^{-1}, respectively.

Obviously, the values of the maximum rate of D4 mass transfer in the biotrickling filter calculated above have large

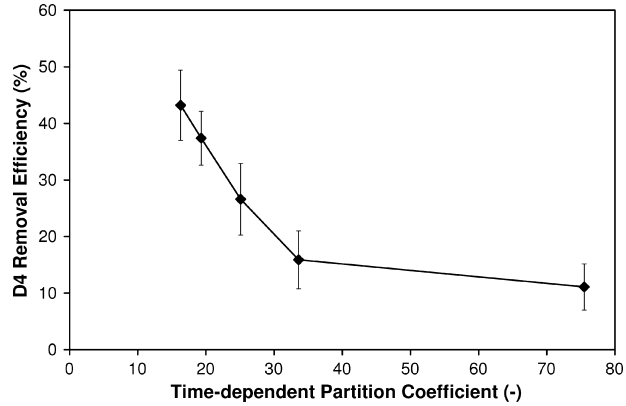

FIGURE 3. Effect of time-dependent dimensionless partition coefficient of D4 between air and mineral medium on the EBRT-dependent performance of the aerobic biotrickling filter. Errors bars are the standard errors.

uncertainties, and they should not be smaller than the observed elimination capacity. However, the fact that the calculated maximum mass transfer rate is markedly lower than the loading imposed during all experiments and is relatively close to the observed elimination rate of D4 indicates that mass transfer is a major rate-limiting factor in biotrickling filters and severely affected D4 removal performance. This stimulated a series of experiments to tentatively increase D4 mass transfer.

Improving Performance Through the Use of a Second Liquid Phase. One possible way to improve the performance of bioreactors limited by mass transfer is to use a nonmiscible nonaqueous liquid phase, which has a greater affinity for the pollutant (*20, 33, 34*). The nonaqueous liquid phase should be biocompatible and nonbiodegradable to sustain performance over extended periods of time. Over the past few years, several groups have reported greater performance for the removal of pollutants difficult to degrade with bioreactors, using a second nonmiscible liquid phase. van Groenestijin and Lake (*35*) reported a 90% removal efficiency for 10 g m^{-3} hexane from off-gases in a biotrickling filter, using silicone oil as the nonaqueous phase. Djeribi et al. (*36*) reported a maximum removal efficiency of 97% and elimination capacity of 537 g m^{-3} h^{-1} for styrene in a biotrickling filter in which 20% silicone oil was added. Kan and Deshusses (*20*) reported that adding oleyl alcohol as an organic nonaqueous phase in a foamed emulsion bioreactor resulted in an increase of toluene elimination capacity of toluene from about 165 to 240 g m^{-3} h^{-1} for high concentrations of toluene inlet, suggesting that the use of a second liquid phase could also help reducing toxicity of the pollutant to the microorganisms when present in high concentrations. The significant improvement in the removal of hydrophobic pollutants when using bioreactors containing two nonmiscible liquid phases suggested the use of the same concept for possibly improving the removal of D4. Thus, a biotrickling filter was operated with an organic emulsion as the trickling phase. Oleyl alcohol was selected as the nonaqueous liquid because of its biocompatibility and nonbiodegradability (*20, 37*). Prior to the setup of the reactor, partition of D4 between air and oleyl alcohol was determined. It was found that D4 partitions into oleyl alcohol much faster than into water or mineral medium, and the partition coefficient was on the order of 1×10^{-2}, which is 100 times lower than that for water or mineral medium. Thus, significant enhancements of mass transfer could be expected.

The biotrickling filter containing the emulsion was monitored for three months at EBRTs of 2 and 4 min. It was found that the reactor was able to remove 70% of D4 for the first week of operation when the EBRT was 2 min. This removal, however, was not sustainable, as during the following days, the removal dropped to as low as 10%. The higher RE observed in the first few days was the result of absorption of D4 into the organic phase of the emulsion. Following analysis of the reactor at an EBRT of 4 min showed no significant improvement in the removal compared to the single liquid phase biotrickling filter, with only a maximum of 20% RE observed. Over time, oleyl alcohol was biodegraded and the stable operation of the biotrickling filter was compromised.

It is obvious that the absorption capacity and the rate of mass transfer was improved by the presence of the organic phase. Even so, the rate of D4 biodegradation remained very slow and thus no improvement of performance was observed compared to the conventional reactor system. Such a result has been observed by other researchers when treating hydrophobic pollutants that are difficult to degrade because of conditions causing biological limitations. Fazaelipoor and Shojaosadati (*38*) saw very little improvement in removing *n*-hexane when using silicone oil as the second liquid phase compared to a conventional biofilter. Cesario et al. (*33*), while evaluating the feasibility of using a nonaqueous liquid phase in bioreactors, suggested that the concept could be applied effectively only when the performance is not limited by the rate of biological reaction.

Overall, the investigations on the use of oleyl alcohol suggested that the mass transfer of D4 to the microorganisms can be improved but that significant kinetic limitations may occur. D4 is a synthetic compound not naturally present in the environment. Microorganisms that will be able to effectively degrade it will take time to evolve and change their metabolic pathways to use D4 as a primary carbon and energy source. In this context, using sludge from facilities producing siloxanes may help obtaining more effective cultures, because the microorganisms present will have already adapted to VMSs.

Supporting Information Available

Schematic diagram of the biotrickling filters removing D4, table of time-dependent partition coefficients of D4 between gas and liquid phases (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

Appendix A

List of Symbols

A	Interfacial contact area in shake flasks (m^2)
a_{btf}	Specific area of the biotrickling filter (m^2 m^{-3})
C_G	Gas phase concentration of D4 (mg m^{-3})
C_L	Liquid phase concentration of D4 (mg m^{-3})
C_G^*	Time-dependent gas phase concentration of D4 (mg m^{-3})
C_L^*	Time-dependent liquid phase concentration of D4 (mg m^{-3})
D_p	Average particle diameter of biotrickling filter bed packing (m)
k_L	Liquid film mass transfer coefficient of D4 (m h^{-1})
$\hat{m}_{D4}$	Maximum D4 mass transfer rate per unit volume of biotrickling filter (mg m^{-3} h^{-1})
P	Time-dependent dimensionless partition coefficient of D4 (−)
V_G	Volume of gas headspace in shake flasks (m^3)

Greek Symbols

ε	Biotrickling filter bed porosity (−)

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Supporting Information for

Biological Removal of Siloxanes from Landfill and Digester Gases: Opportunities and Challenges

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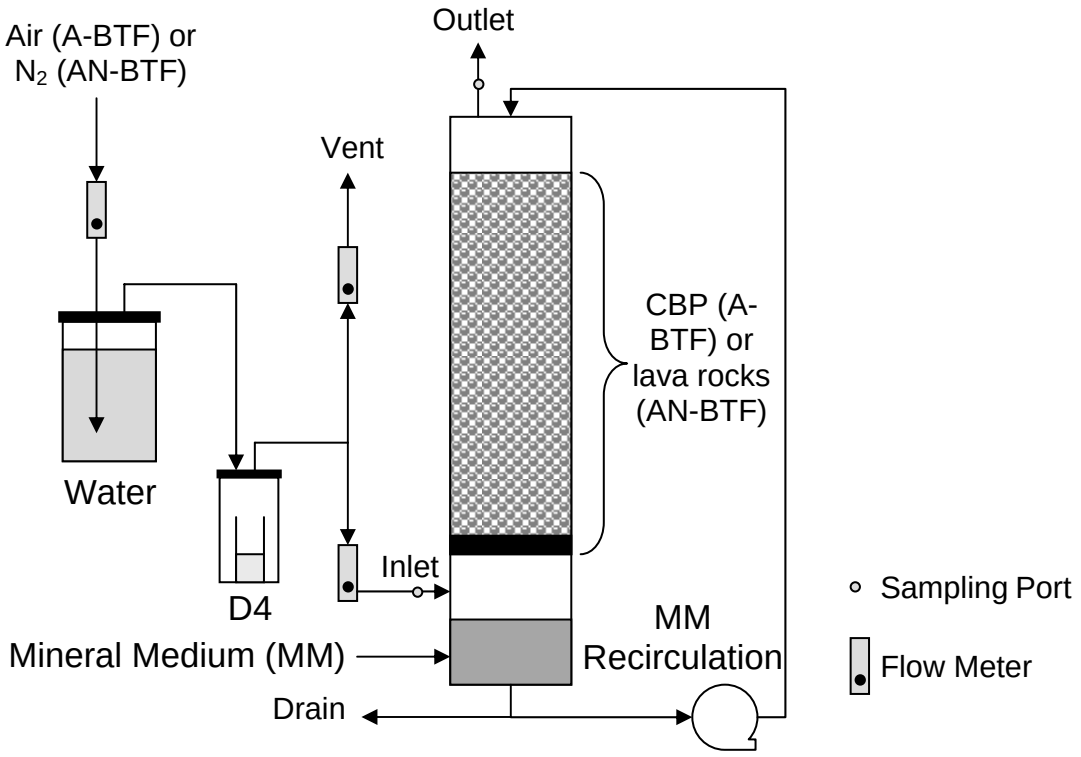

Figure S1. Schematic diagram of the biotrickling filters removing D4. A-BTF = aerobic biotrickling filter; AN-BTF = anaerobic biotrickling filter.

Table S1. Effect of the equilibration time on the partition of D4 between gas and liquid phases. Uncertainties reported are the standard errors.

Equilibration Time (h)	D4 Partition Coefficient (-)			Toluene Air-Water Partition Coefficient (-)
	Air-Water	Air-Mineral Medium	Air-Cell Suspension	
0.26	-	19.3 ± 6.4	-	-
0.32	-	16. 4 ± 3.6	4.6 ± 0.7	0.34 ± 0.09
1	10.2 ± 0.8	9.3 ± 1.5	4.1 ± 0.4	0.27 ± 0.08
2	3.1 ± 0.3	5.7 ± 1.0	4.0 ± 0.5	0.28 ± 0.05
4	2.8 ± 0.4	5.5 ± 0.8	-	0.3 ± 0.08
16	1.8 ± 0.1	5.2 ± 1.0	-	-
24	1.6 ± 0.2	5.3 ± 0.9	-	-