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Study on Degradation of Octamethylcyclotetrasiloxane (D4) in a Biotrickling Filter under Aerobic Conditions

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Octamethylcyclotetrasiloxane (D4) is a volatile organosilicon compou[illegible]sent in biog[illegible]roduced by widely using industrial and consumer products. Due to being harmful to many organisms at very lo[illegible]ntrati[illegible]nd forming SiO_2 deposits during biogas combustion, degradation of D4 in biotrickling filter was investigated. The deg[illegible]ture of D4 was taken from the effluent of an organic silicon manufacturer. The culture was inoculated in [illegible]trickling filter. Effects of pH, the D4 inlet concentration in the synthetic gas, empty bed residence time and liquid flowrate on D4 re[illegible]e investigated. The results showed the optimum pH for D4 degradation was 6.7. The high D4 removal efficiency of 55.3[illegible]d the h[illegible]ination capacity of 148.5 mg m^{-3} h^{-1} were obtained.

Keywords: Octamethylcyclotetrasiloxane (D4), Biodegradati[illegible]ms, Separation, Purification, Identification.

INTRODUCTION

A variety of volatile methylsiloxa[illegible]MSs) released into the environment due to the wi[illegible]of organo-silicon compounds in industrial [illegible]consum[illegible]ducts[1,2]. Cyclic volatile methylsiloxanes[illegible]MS) are a su[illegible]of volatile methylsiloxanes incli[illegible]olatilizing into atmosphere due to their high vapo[illegible]ssu[illegible]water solubilities and high Henry's Law consta[illegible]s. Octamet[illegible]otetrasiloxane (D4) is the most abund[illegible]for 60 % in all t[illegible]lic volatile methylsiloxane and th[illegible]4 concentrations in landfill gas have been reported of up[illegible]40 m[illegible].

Not only D4[illegible]biogas[illegible]s notew[illegible]thy environmental loadings, but also[illegible]uced fro[illegible]ndfill pools and the effluent of wastewater t[illegible]at plant[illegible]s been limited[2-4], as D4 could conve[illegible]iO_2 depos[illegible]e surfaces of gas engines or boiler[illegible]te[illegible]eral millim[illegible]s thick during the energy produc[illegible]proces[illegible]which leads to a decrease in heat exchange effici[illegible]y and ar[illegible]intenance costs[7,8]. As a result, to remo[illegible]lin[illegible]e D4 from the biogas is an urgent need[4].

So fa[illegible]technologies of gas adsorption, absorption and deep chilli[illegible]been commercialized to remove siloxanes from biogas[8-10]. I[illegible]physical adsorption, most adsorbents are not siloxane-selective, some adsorbents are not regenerable and the regenerable adsorbents are costly if regenerable. In chemical absorption, siloxanes are destroyed by strong bases [illegible]acids, but the application of chemical absorption agents is [illegible]ssociated with safety[9]. For physical absorption, the variation of siloxanes concentrations in landfill or digester gas might lead to desorption at low concentration or elevated gas flow rates[11]. Deep chilling is generally regarded as economically suitable only at high flow rates and elevated siloxanes load[12,13]. A new research in biogas purification is focused on biological processes which are attractive from an economical and technological point of view[14].

Many researchers have studied the D4 biodegradation process for removal of octamethylcyclotetrasiloxane (D4) from biogas. Deshusses *et al.*[14a] found when D4 concentrations were controlled in the scope of 45 ± 5 mg m^{-3} in the gas phase, the removal of D4 in the aerobic biotrickling filter reached 43 % at an empty bed residence time (EBRT) of 19.5 min[2]. According to Accettola *et al.*[15], when D3 concentration was 45 mg m^{-3}, the removal efficiency was well above 10 %[15]. Grümping *et al.*[16] reported that only approximately 3 % of the added D4 was degraded after 100 days of incubation.

The main objective of this work is to verify whether there are strains capable of degrading D4 well in nature. In this study, activated sludge was taken from the effluent of Inner Mongolia Hengyecheng organic silicon Company Limited. Biotrickling filter (BTF) was used as the equipment for degrading D4. Continuous experiments were carried out to investigate the effect of D4 degradation.

EXPERIMENTAL

Culture media: The culture media for the microorganisms consisted of 1 g L^{-1} K_2HPO_4, 1 g L^{-1} KH_2PO_4, 1 g L^{-1} KNO_3, 1 g L^{-1} NaCl, 0.2 g L^{-1} $MgSO_4$, 0.026 g L^{-1} $CaCl_2{\cdot}2H_2O$ and 2 mL L^{-1} solution of trace elements and D4 (purity, > 99 %; purchased from Shandong Dayi chemical industry Co., Ltd) of 0.5 mg L^{-1} were also added. The final pH of the mixture was adjusted to 6.70-6.80.

Experimental setup: In order to investigate the removal efficiency of D4, a technological process containing biotrickling filter was set up as shown in Fig. 1. The air from the cylinder was split into two, one went forward on its own and the other went to a bottle with a lid containing D4. Mimic synthetic gas containing D4 was produced after two streams met in a mixer packed with ceramic ring.

The biotrickling filter was made of glass, the height of which was 1 m and the diameter was 50 mm. The inert packing material in the biotrickling filter was polypropylene cascade ring of 4-6 mm. The biotrickling filter was inoculated initially with 400 mL of enriched batch cultures and 1600 mL of fresh nutrient medium. The initial pH of the recirculating liquid in the biotrickling filter was 6.7-6.8. The culture liquid was recirculated from the bottom to the top of the column using a booster pump (flow rate 10 L h^{-1}) to provide the bacteria with moisture and minerals necessary for growth. Circulating liquid of 1600 mL was replaced by fresh nutrient medium every week. Synthetic gas containing D4 flowed through the colu counter-current with the recirculating medium.

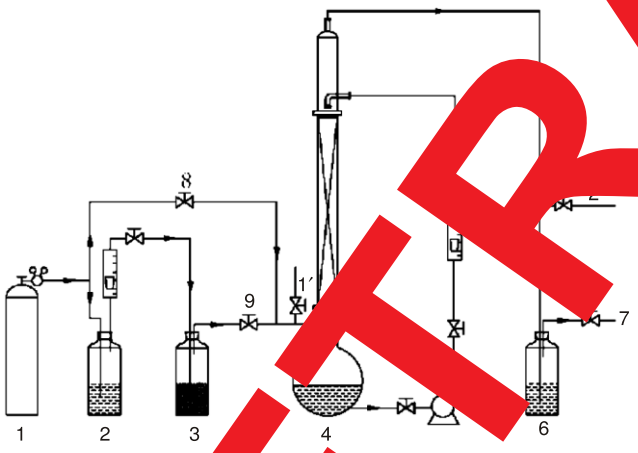

Fig. 1. Schematic of th eriment tup, 1. Air cylinder; 2. D4 bottle; 3. mixer; 4. bi kling fil . Booster pump; 6. Emptying; 7-9. Value; 10-1 flowm , 13. Liq owmetre; 1'. Inlet gas sampling; 2 mpling.

Analyti ethods. n rate of batch cultures was obta asuring tu ty at 1 h intervals using a UV-21 pectro otometer (UNICO, China) at 600 nm.

gas con 04 in gas phase were measured on a ies II gas chromatograph fitted with a 30 m × 0.32 m 25 μm HP-5 column. The carrier gas was N_2 and the detec a flame ionization detector. A 1000 μL injection syringe used for injecting gas samples into the vaporizer. The vaporizer temperature: 190 °C, the column temperature: 145 °C. The retention time of D4 under these conditions was 3.5 min and the detection limit was 1 mg m^{-3}.

Metabolites of D4 in the recirculating liquid need to be completely extracted into an salts solution of tetrahydrofuran (THF) for structural identification by GC-MS. The extraction efficiency was estimated to be 95 %. It s pointed out that although THF is completely mis with it did form a separate layer when the dis d salts are p t. A sample taken from recirculat quid was ex ted repeatedly. Anhydrous $MgSO_4$ crys added i the combined extracts to remove er. Final F s t was removed using a rotary e orator and the s liquid residues were degradatio oducts D4. Beca e silanols with two hydroxy gr per S om do t survive and couldn't be eluted from under t GC conditions, silanol functions o e meta need e protected using a trimethyl-silyl agent call thylsilyl)trifluoro-acetamide (BS) before GC-MS lysis[17]. Degradation products of tected by an East-West Series 4000A Gas Chro ograph d with VG ZAB-HS High Resolution Magnetic mass spec er. GC systems were equipped with a × 0.2 mm × 0. μm SE-30 column. GC-MS co were as follows: MS source temperature, 200 °C; M uadrupole tem erature, 100 °C; GC: initial temperature, 3 C; initial time min; heating rate, 10 °C min^{-1}; heating ti 15 min; final perature, 180 °C for 60 min[17].

ic acid is based on the reaction of dissolved silicate onium molybdate in an acidic solution to form yellow coloured silicomolybdic acid. If ascorbic acid is blue dye called silicomolybdenum blue is formed an ty of silicic acid can be determined by detecting t bsorbance of silicon molybdenum blue solution at 810 using a spectrophotometer (UV-2100 Spectrophotometer, NICO, China)[18].

RESULTS AND DISCUSSION

Effect of pH, D4 inlet concentration in the mimic mixed gas, EBRT and liquid flow on process performance: The removal efficiency (RE) and the elimination capacity (EC) of D4 were respectively evaluated by $EC = (QC_{in}-QC_{out}-\Delta C_{liq}L_{liq})/V$ and, $EC = (QC_{in}-QC_{out}-\Delta C_{liq}L_{liq})/V$ where C_{in} (mg m^{-3}) is D4 inlet concentration, C_{out} (mg m^{-3}) is D4 outlet concentration, Q is the gas flowrate (m^3 h^{-1}), V (m^3) is the empty volume of the biotrickling filter and ΔC_{liq} (mg L^{-1} h^{-1}) is the change of D4 concentration in liquid phase per unit time and L_{liq} (L) is the volume of circulating fluid in the biotrickling filter.

The biotrickling filter was initialized by inoculation with the enriched culture. The mineral medium of 2 L was circulated in the biotrickling filter at a flow of 10 L h^{-1}. The synthetic gas containing D4 was guided through the column in counter-current with the circulating liquid. The experiment was carried out for 106 days.

As can be seen in Fig. 2, until day 35, D4-degrading bacteria had been successfully enriched in the biotrickling filter and high D4 removal efficiency were achieved at different pH (area A), D4 inlet concentration (area B), different EBRT (area B) and different liquid flow (area C).

Fig. 2 shows the influence of pH on D4 removal efficiency at EBRT of 15 min, the liquid flow of 10 L h^{-1} and D4 inlet concentration of 50, 100, 150 and 200 mg m^{-3}. In case of the

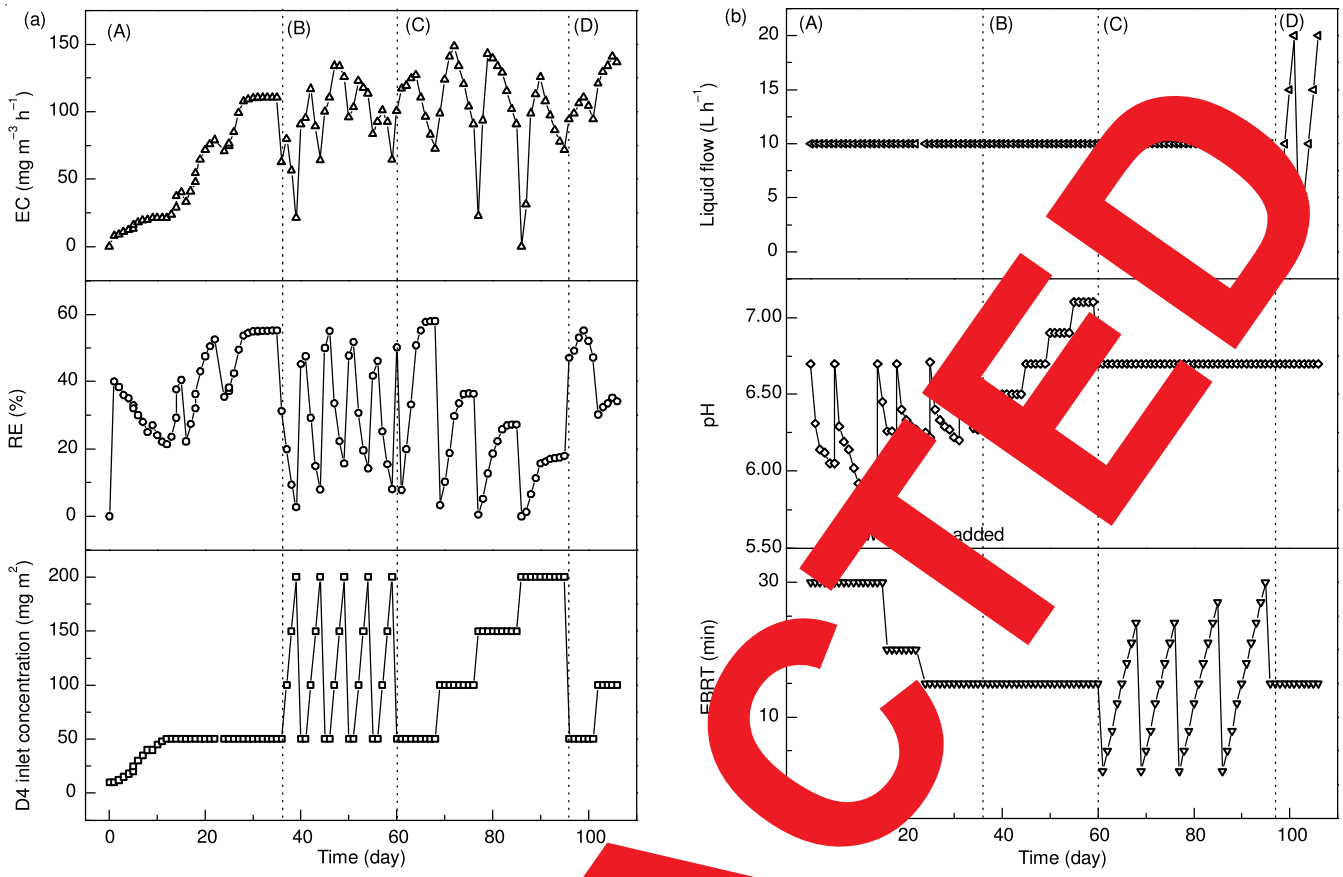

Fig. 2. Influence of pH, EBRT, D4 inle liquid flow on process performance

other conditions are the same, no matter how much was th D4 inlet concentration, removal efficiency was largest at pH of 6.70. When the D4 inlet concentration ren mg m^{-3} and the liquid flow was 10 L h^{-1}, removal e ency i eased from 7.8 % at EBRT of 2 min to 55.3 % EBRT followed by keeping constant nearly. EBRT and RC achieved to the maximum value 12 m^{-3} h^{-1} at EBRT of 12 min. Removal efficien ecreased D4 inlet concentration increasing at the s EBRT. The m EC was 148.5 mg m^{-3} h^{-1}. D4 remo ency first rose and then fell with the increase of liqui w. removal efficiency was strongly dependent on pH, the ini oncentration, EBRT and the liquid f The reduction o RT and the increase of the D4 in oncentration resulted in the decline of removal efficien

D4 removal ciency tained m our continuous experiment was h at in pre s studies. So attractive degradation effec tained be due to the bacteria originated f e sewag f organic silicon manufacturer.

Si the c nuous experiments were initiated, pH decr d with with final value of below 6. The i nts on the curve in Fig. 2 are the time when fresh nutr lution was added. The reduction of pH may be the result ducing silicic acid or nitrate during D4 metabolism.

Biodegradation products of D4: When the mixture gas containing D4 flowed through the biotrickling filter, degradation products of D4 entered the recirculation liquid.

ee samples were, respectively taken from the kettle of the otrickling filter, the fresh nutrient and the deionized water. icic acid tests were performed respectively. As presented in . 3, No. 1, 2 and 3 were the silicic acid test results of the ecirculation liquid, the fresh nutrient and deionized water, respectively. It can be seen that the difference among the three pictures is obvious. No. 3 had the lightest colour, No. 2 was deeper than it and No. 1 was the deepest one among them. It is suggested that a large number of silicic acid was contained in the recirculation liquid of the biotrickling filter. It can be inferred that abundant silicic acid was produced due to D4

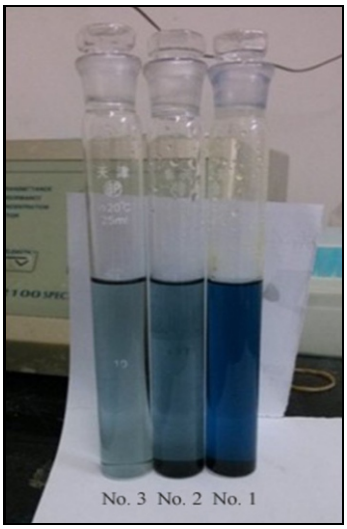

Fig. 3. Experimental photos which proved silicic acid was generated

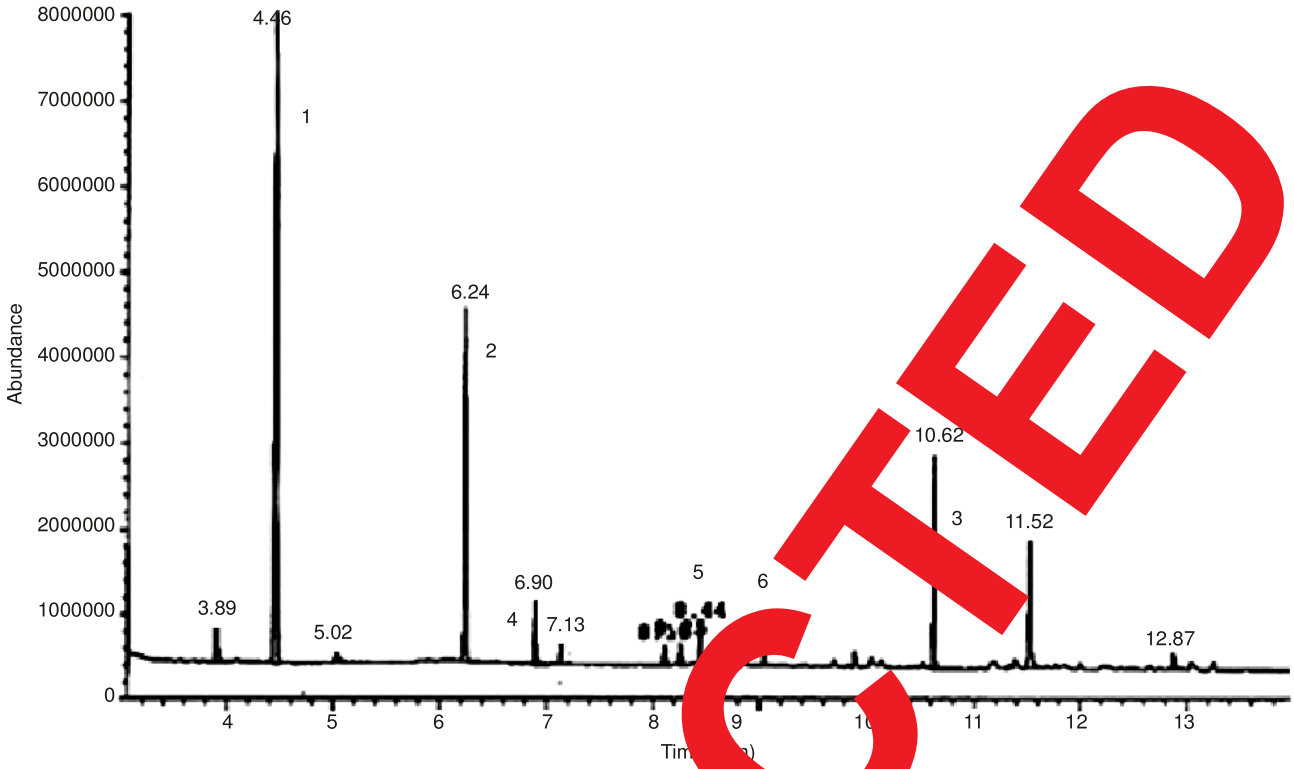

Fig. 4. Gas chromatogram of the BSTFA products from D4 metabolites in the recir[illegible]iquid [illegible]biotrickling filter, 1. Me_3Si-O-$SiMe_2$-O-$SiMe_3$; 2. D4; 3. Me_3Si-O-$(CO)_2$-O-$SiMe_3$; Me_3Si-$(O$-$SiMe_2)_2$-O-$SiMe_3$; 5. D5; 6. Si(O-Si[illegible]

degradation by the bacterial strain when the gas flowed th[illegible] the biotrickling filter.

Degradation products of D4: The profile of BSTF[illegible] derivatization products from D4 metabolites was obtained using GC equipped with MS. As shown in F[illegible] the GC spectrogram revealed five organic silicon co[illegible]e one major compound, constituting more than[illegible]% of [illegible] total compounds, was identified as Me_3Si-O-[illegible]Me_2-O-[illegible]. The minor compounds identified were Me_3Si-([illegible]-$SiMe_3$, Me_3Si-O-$(CO)_2$-O-$SiMe_3$, D5, Si(O[illegible]$Me_3)_4$ [illegible]on.

The species detected by GC[illegible]MS were i[illegible]meta-bolic products themselves but[illegible]BSTFA derivati[illegible]Ac-cording to the BSTFA deriva[illegible]cedure, it can be in-ferred that the one major D[illegible]metabo[illegible]HO-$SiMe_2$-OH and the minor D4 metab[illegible]ites were HO-Si[illegible]$SiMe_2$-OH, Me_3Si-$(CO)_2$-O-$SiMe_2$[illegible], $Si(OH)_4$, *etc.*

Conclusion

The activate[illegible]udge t[illegible]n from [illegible] effluent of Inner Mongolia Hengy[illegible]anic sili[illegible]Company Limited exhibited favorable pe[illegible]nce in[illegible] biotrickling filter for D4 degrada[illegible]d remova[illegible]y of 55.3 % was achieved and the [illegible]el[illegible]ation capa[illegible] of 148.5 mg m^{-3} h^{-1} was obtain[illegible]he de[illegible]dation products of D4 were identified as HO-[illegible]$_2$-OH, [illegible]Me_2-OH, $Me_3SiO(CO)_2OSiMe_3$, D5, S[illegible]The degradation pathways and mechanism for the for[illegible]of the various metabolites were also supposed.

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[illegible]re also due to members from the laboratory of Prof. W[illegible]g for their help and advice in the process of strain i[illegible]tion and identification.

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