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Biofiltration of 1,1,1-Trichloroethane by a Trickle-Bed Air Biofilter

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Abstract

The performance of a trickle-bed air biofilter (TBAB) in the removal of 1,1,1-trichloroethane (TCLE) was evaluated in concentrations varying from 0.025 to 0.049 g/m^3 and at empty-bed residence time (EBRT) varying from 20 to 90 s. Nearly complete TCLE removal could be achieved for influent carbon loading between 0.98 and 5.88 $g/m^3 h$. The TBAB appeared efficient for controlling TCLE emission under low-carbon-loading conditions. Carbon recoveries higher than 95% were achieved, demonstrating the accuracy of results. The carbon mass rate of the liquid effluent was approximately two orders of magnitude less than that of the effluent CO_2, indicating that dissolved TCLE and its derivatives in leachate were present in negligible amounts in the TBAB.

Index Entries: Biofiltration; trickle-bed air biofilter; 1,1,1-trichloroethane; empty-bed residence time; influent concentration.

Introduction

1,1,1-Trichloroethane (TCLE) is a commonly used industrial chemical. In addition to its use as a solvent, it is frequently encountered in the semiconductor industry, optoelectronic industry, pharmaceutical industry, and chemical industry. Because of the lack of proper air pollution control devices, many TCLE vapors are released into the atmosphere during the manufacturing process every year. The release of TCLE into the atmosphere may have an adverse effect on nervous system, liver, and heart of humans *(1)* and thus endanger public health and welfare. TCLE is also an ozone-depleting substance. The feature of the Montreal Protocol requires that the production and consumption of TCLE be controlled and eliminated *(2)*.

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More stringent requirements for the removal of volatile organic compounds (VOCs) from waste gases in recent years necessitate the development of innovative, cost-effective treatment alternatives. Traditional VOC control technologies such as carbon adsorption, liquid scrubbing, condensation, thermal incineration, and catalytic incineration have been commonly used to remove VOC vapors from waste gases. However, these VOC control technologies may suffer from high operating costs and secondary waste-stream issues *(3)*.

The biofiltration process is a relatively new application that has been proven more cost-effective than traditional technologies for treating low-strength and some high-strength VOCs *(4)*. The system consists of a filter bed usually filled with natural organic media such as peat, compost, leaves, wood bark, and/or soil. The bed moisture is kept at a constant level by humidification of influent air to maintain a biologically active layer surrounding the medium, known as the "biofilm" *(5)*. VOC-containing waste gases are transported to the air–biofilm interface, where they are absorbed into the biofilm and employed as carbon and/or energy sources by the micro-organisms. The trickle-bed air biofilter (TBAB) employs synthetic, inorganic media and receives liquid nutrients through a spray nozzle system on the top of the TBAB. Because of better control of the pressure drop across the bed, pH, and nutrient feed, TBABs allow for more consistent operation and do not suffer the effects of aging as natural media do *(6)*.

The TBAB has been proven to be very efficient for treating many kinds of VOCs such as benzene, toluene, ethylbenzene, xylene *(6,7)*, styrene *(8,9)*, acrylonitrile *(10)*, *N*-dimethylacetamide *(11)*, methyl acetate *(12)*, and ethyl acetate *(13)*. However, quantitative information regarding the biofiltration of TCLE vapor is still unavailable in the literature. There have been studies on TCLE biodegradation in liquid suspension systems *(14)* and in a granular activated carbon (GAC) column where TCLE is in the liquid phase *(15)*.

This research aims at evaluating the TBAB performance in the treatment of air contaminated by TCLE in concentrations varying from 0.025 to 0.049 g/m^3 and at empty-bed residence time (EBRT) varying from 20 to 90 s. Experimental results obtained herein provide useful information concerning the design criteria and operation of a full-scale TBAB for controlling TCLE emission.

Materials and Methods

Experimental Setup

The experimental setup of the TBAB used for TCLE removal is shown in Fig. 1. It was made of glass and had length of 100 cm and internal diameter of 10.85 cm. A 10-cm head space was designed for the TCLE waste-gas inlet and for housing a nutrient spray nozzle, and a 10-cm bottom space was designed for the outlet of treated air and leachate. The TBAB was filled with 7.86 L of packing material consisting of coal particles with a density of 0.318 kg/L, equivalent-volume diameter of 2 cm, average pore

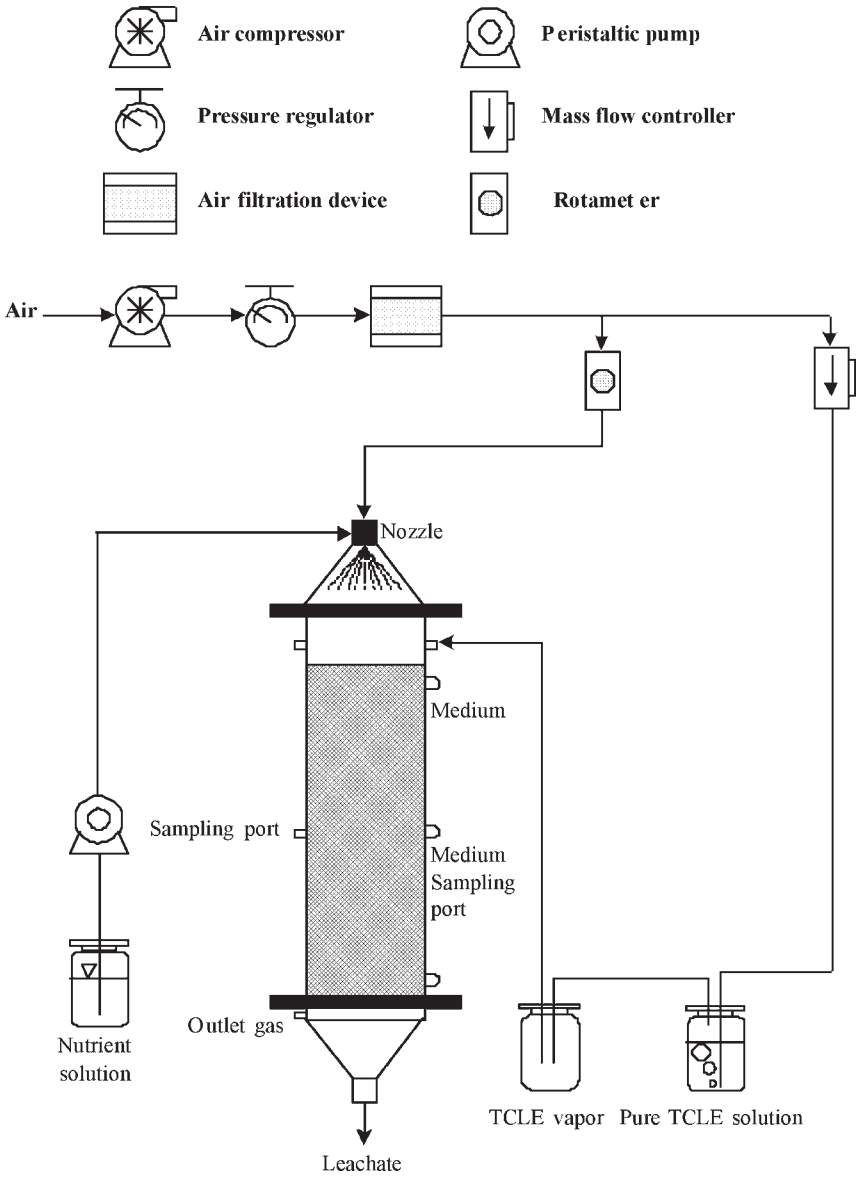

Fig. 1. Schematic diagram of the trickle-bed air biofilter for the removal of 1,1,1-trichloroethane.

size of 23.25 µm, and surface area of 6.21 m^2/g (BET analyzer, ASAP 2000; Micromeritics, USA). The void fraction before biofilm attachment was 44% of the packed volume. The temperature inside the TBAB was not controlled through the study to simulate the performance of real-scale uncontrolled biofilter.

Compressed air was passed first through a filtration device (LODE STAT compressed air dryer, Model LD-05A, Taiwan) to remove moisture,

Table 1
Chemical Composition
of the Nutrient Feed for a Carbon Loading
of 0.98 g C/m^3 h (Run 1)

Constituents	Concentration
KNO_3 (g/L)	0.03
$Na_2HPO_4 \cdot 12H_2O$ (g/L)	0.01
$(NH_4)_2SO_4$ (g/L)	0.01
KH_2PO_4 (g/L)	0.01
$FeSO_4 \cdot 7H_2O$ (mg/L)	0.56
$CaCl_2 \cdot 2H_2O$ (mg/L)	3.00
$MgSO_4 \cdot 7H_2O$ (mg/L)	2.00
$Na_2MoO_4 \cdot 2H_2O$ (mg/L)	1.00
$MnSO_4 \cdot H_2O$ (mg/L)	0.88
$NaHCO_3$ (g/L)	1.50

oil, and particulate matter. After purification, the major airstream was mixed with a 2.4-mL/min nutrient solution and delivered into the head space by a nozzle spray system. The minor airstream was passed through two glass bottles containing pure TCLE solution (JT Baker, Actual Analysis, USA; 99.9% purity) and air, respectively, to produce TCLE vapor. The TCLE vapor was then mixed with the major airstream in the head space and passed into the bed with the flows directed downward. The major airstream rate was regulated by a rotameter, and the influent TCLE concentration was controlled by regulating the minor airstream flow rate using mass flow controllers (MKS, Model 247C, Andover, MA). The variations of influent TCLE concentration were within 10%. The nutrient feed contained inorganic salts and $NaHCO_3$ as a buffer. The nutrient was feed by a peristaltic pump from a 20-L nylon bottom at a 3-L/d flow rate. The carbon mass ratio of influent TCLE to nitrogen, phosphorus, sulfur, and iron of nutrient solution was equal to 100:10:1:1:0.5. The composition of nutrient solution for a carbon-loading rate of 0.98 g C/m^3 h (Run 1) is listed in Table 1, whereas those of other runs were proportionally increased or decreased according to the carbon-loading ratio of influent waste gas to that of 0.98 g C/m^3 h. In order to test the buffer capacity of TCLE on coal particles, adsorption and desorption experiments were carried out before the TBAB start-up. For the adsorption experiment, the reactor was fed at 7.86 L/min (EBRT = 60 s) using an airstream containing 0.49 g/m^3 TCLE. The influent and effluent TCLE concentrations were monitored every 0.5 h. For the desorption experiment, the TBAB was operated at 15.72 L/min (EBRT = 30 s) pure air. The effluent TCLE concentration was monitored every hour.

The TBAB was seeded with activated sludge having suspended solid (SS) and volatile suspended solid (VSS) contents of 42.07 g/L and 7.78 g/L, respectively, which was obtained from the sludge thickener of a wastewater treatment plant in Hsinchu Science-Based Industry Park (Hsinchu,

Taiwan). Suspended solids were allowed to settle for 4 h and the supernatant was discarded to obtain concentrated sludge. The seeding step consisted of mixing 500 L of concentrated sludge with coal particles and 125 g $CaCO_3$. The addition of $CaCO_3$ was used to prevent acidification inside the TBAB. Coal particles with biological attachment were placed into the TBAB for about 3 h. After microbial seed, the TBAB was fed with a 2.4-mL/min nutrient solution at a 5.24-L/min flow rate (EBRT = 90 s) containing 0.1 g/m^3 TCLE.

Analytical Methods

The TCLE concentrations in the airstream were measured using a gas chromatograph (GC) (China Chromatography 8900 Series, Taiwan) equipped with a flame ionization detector (FID). A 60-m SUPELCOWAX fused-silica capillary column (0.32 mm inside diameter, 1 µm film thickness) was used. Sampling ports were located at the inlet, outlet, and middle height of the TBAB. A 0.5-L effluent air sample was collected using a 1.0-L Teflon bag (SKC Inc., Pennsylvania, USA). Air samples (0.1 mL) were taken in this bag using a gas-tight syringe and injected into the gas chromatograph. The GC-FID was operated at an injection temperature of 150°C, a detector temperature of 200°C, and an oven temperature of 150°C.

The following parameters were determined according to Standard Methods *(16)*: soluble chemical oxygen demand (SCOD, 5220-D), SS (2540-D), and VSS (2540-G). The pH values of nutrient solution and leachate were measured by a digital pH meter (SUNTEX SP-701, Taiwan). The CO_2 concentration in the airstream was determined by a CO_2 analyzer (TESTO Model 535, Germany). The pressure drop across the bed was measured using an oil-filled manometer (Dwyer Model 400, Michigan, USA).

A pair of tweezers was used to remove coal particles from the TBAB. The mass of the attached biofilm per unit volume of coal particles (X_a) was evaluated by drying coal particles before and after biofilm attachment at 80°C for 24 h. The difference between the two measurements divided by the volume of the coal particle was equal to X_a.

Carbon Balance Analysis

Carbon balance was performed after the achievement of pseudo-steady-state conditions in each run. It can be written as

$$Q_a C_i = Q_a C_e + Q_a C_c + \alpha Q_l C_b + \beta Q_l C_l \quad (1)$$

where Q and C represent the flow rate and carbon concentration, respectively, $Q_a C_i$ and $Q_a C_e$ are the influent and effluent carbon mass rates associated to TCLE, $Q_a C_c$ is the effluent carbon mass rate associated to CO_2 production, $\alpha Q_l C_b$ is the biomass production rate equivalent to the carbon utilization rate, and $\beta Q_l C_l$ is the effluent carbon mass rate of the leachate. Assuming that the net accumulation of attached biomass in the TBAB was negligible (i.e., biomass production rate = biofilm detachment rate), the C_b

Table 2
Operating Conditions of Continuous Tests of TCLE Removal in TBAB

Run no.	C_i (g/m^3)	Q_a (L/min)	EBRT (s)	L (g/m^3 h)
1	0.025	5.24	90	0.98
2	0.025	7.86	60	1.47
3	0.049	5.24	90	1.96
4	0.049	7.86	60	2.94
5	0.025	15.72	30	2.94
6	0.025	23.58	20	4.41
7	0.049	15.72	30	5.88

Note: C_i = TCLE concentrations in the inlet gas phase; Q_a = air flow rate; L = carbon loading referred to the biofilter volume.

level can be estimated from the VSS of the leachate. Because the predominant micro-organisms in the biofilter decomposing VOCs are heterotrophic bacteria and fungi *(17)*, $NaHCO_3$, which was added into the nutrient solution as a pH buffering compound, was not included in the carbon balances. A typical cellular composition for a heterogeneous microbial population can be represented as $C_5H_7NO_2$ *(18)*; therefore, the conversion factor of biomass to carbon concentration, α, can be assumed to be equal to 0.53 (60/113). The C_l level can be approximated from the SCOD of leachate; the conversion factor of SCOD to total organic carbon (β = 0.375) can be evaluated from the stoichiometry for TCLE oxidation:

$$C_2H_3Cl_3 + 2\ O_2 \rightarrow 2\ CO_2 + 3\ HCl \quad (2)$$

The carbon recovery, R, is defined as the percentage ratio of the sum on the right-hand side of Eq. (1) to Q_aC_i.

Experimental Plan

The operating conditions of continuous runs are summarized in Table 2. The experiments were performed by following the order of runs in Table 2. The influent TCLE concentration was selected so as to simulate various emissions from the industries mentioned in the Introduction. The EBRT was varied from 20 to 90 s to establish the optimum operating conditions and the influent carbon loadings were in the range of 0.98 (Run 1) to 5.88 g C/m^3 h (Run 7).

Results and Discussion

Figure 2 shows the breakthrough curve for adsorption of TCLE vapor on coal particles and the curve for desorption of TCLE vapor from coal particles. The effluent TCLE concentration started to increase quickly after 4 h of operation and the influent TCLE concentration could be reduced from 0.49 to below 0.06 g/m^3 by coal particles during this

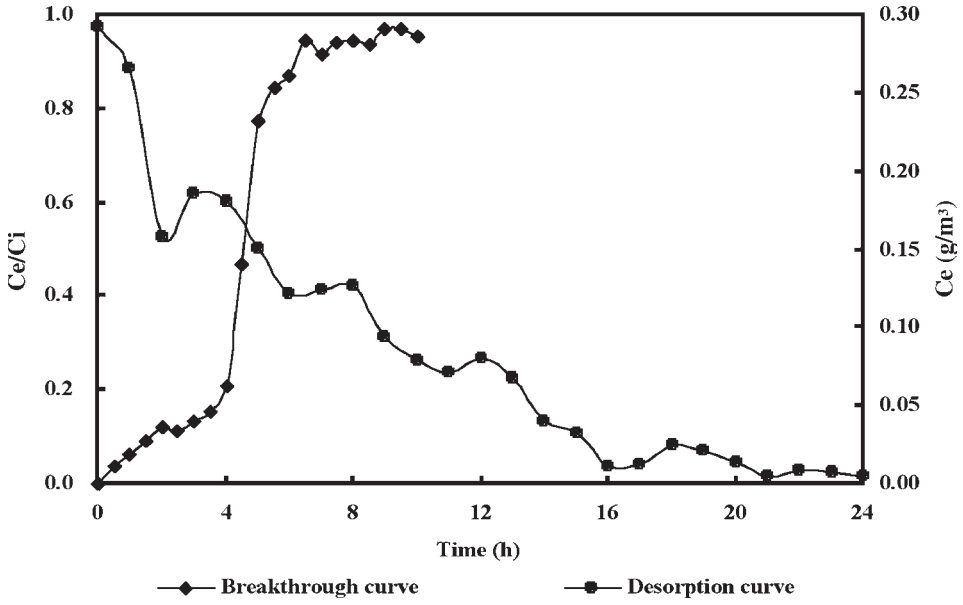

Fig. 2. Breakthrough curve of TCLE vapor on coal particles and desorption curve of TCLE vapor from coal particles.

period. After 8.5 h of operation, the effluent TCLE concentration reached steady values (approx 95% of the influent TCLE concentration). The operating capacity of coal particles to remove TCLE was equal to 4.4 mg TCLE/g coal. The desorption curve indicated that the TCLE was slowly released from coal particles. After 20 h of operation, the effluent TCLE concentration was reduced from 0.29 to 0.01 g/m^3. Based on these results, it could be concluded that the coal particle appeared efficient for buffering the fluctuations in TCLE concentration.

The temperature inside the TBAB, the pH of the leachate, and the influent and effluent TCLE concentrations were monitored every 2–3 d. The temperature inside the TBAB ranged from 16.9°C to 26.8°C, with an average of 21.3°C, and the pH of the leachate ranged from 7.8 to 8.5, with an average of 8.2. Figure 3 shows the TBAB performance in terms of time behaviors of influent TCLE, effluent TCLE, and removal efficiency. With the exception of the start-up period (about 30 d), each run was operated for 1–2 wk to reach the pseudo-steady-state. Pseudo-steady-state was assumed to take place when the changes in the TCLE removal efficiency, as the difference between influent and effluent TCLE concentrations divided by influent TCLE concentration, were within 5% for three successive samples. With the exception of Run 5, the TCLE removal efficiency increased gradually, reached steady values, and then decreased rapidly after a sudden change of EBRT or influent TCLE concentration. Nearly complete TCLE removal could be achieved at the end of each run, indicating that the TBAB could be efficient for controlling TCLE emission under a low-carbon-load-

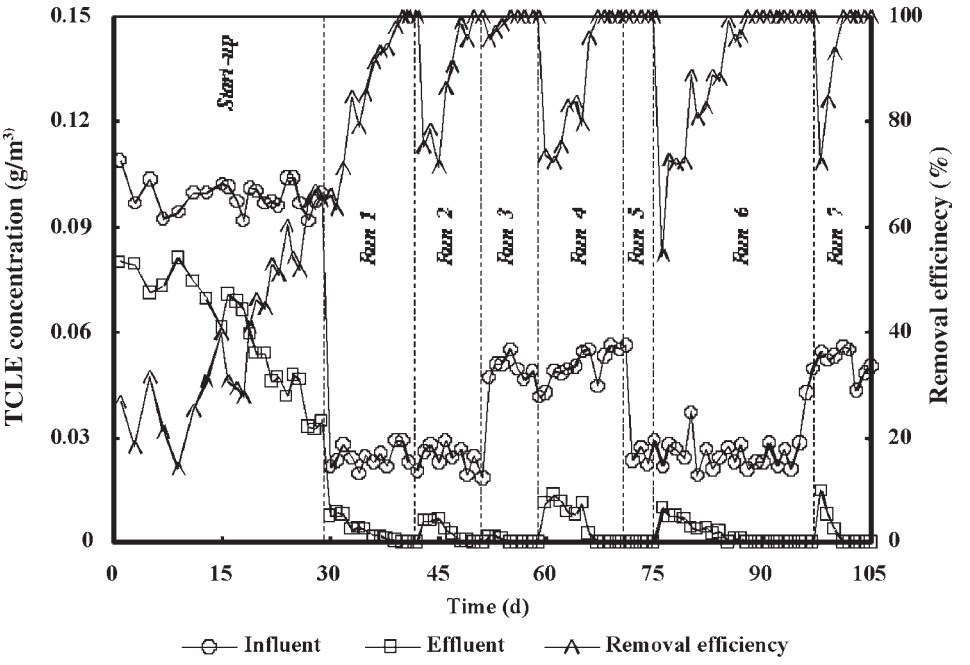

Fig. 3. Performance of the TBAB for TCLE removal.

ing condition. It must be noted that there are no reports in the literature of any micro-organisms capable of degrading TCLE under aerobic conditions as a carbon and energy source. TCLE can be degraded under aerobiosis if a cometabolite is added *(14,15)*. The cometabolite of this study may be from organic compounds dissolved from the coal. This phenomenon is still unclear at the present time and further studies are needed.

The CO_2 concentrations of influent and effluent airstreams were evaluated and are listed in Table 3. The difference between the two concentrations was equal to CO_2 production. The theoretical CO_2 production estimated from Eq. (2), which assumes that all of the carbon in the influent TCLE was converted to CO_2, is also presented. The CO_2 production could be the result of TCLE biodegradation and biomass decay. The data show that fair agreement was observed between the concentrations of measured and theoretical CO_2 production, indicating that most of the CO_2 production was the result of TCLE biodegradation. The measured data were slightly lower than the theoretical results and the discrepancies were in the range 0.04–7.52%, because of three possible reasons. First, some of the TCLE vapor was dissolved into the nutrient solution. Second, some of the TCLE vapor was utilized and converted to microbial cell. Third, some of the CO_2 gas was lost during the analytic determination of this gas. The data also show that, with the exception Run 6, CO_2 production increased as the influent TCLE concentration increased, probably because the biofilter was operated under conditions of carbon source limitation. On the other hand, the changes of

Table 3
Carbon Dioxide Production During Continuous Tests of TCLE Removal in TBAB

Run no.	Influent CO_2 (mg/m^3)	Effluent CO_2 (mg/m^3)	Measured CO_2 production (mg/m^3)	Theoretical CO_2 production (mg/m^3)	Difference (%)
1	196.57	202.94	6.37	6.83	6.73
2	199.51	205.40	5.89	6.19	4.85
3	203.43	217.16	13.73	13.91	1.29
4	205.40	223.04	17.64	18.88	6.57
5	200.00	209.32	9.32	9.65	3.42
6	198.53	213.73	15.2	16.43	7.49
7	199.51	216.18	16.67	16.67	0.00

Table 4
Values of the Main Parameters of TCLE Biofiltration in TBAB

Run no.	X_a (g/L)	P (cm H_2O)	SCOD (mg/L)	Y (g biomass/g TCLE)
1	1.78	0.59	32	0.048
2	1.95	1.08	41	0.022
3	2.11	0.86	45	0.015
4	2.64	1.19	49	0.010
5	2.74	1.85	37	0.017
6	4.29	3.55	82	0.039
7	4.48	2.23	70	0.019

CO_2 production as a function of EBRT were not so evident. The concentrations of CO_2 production were in the range 10–40 mg/m^3.

The results of attached biomass per unit volume of coal particle (X_a), pressure drop across the bed (P), SCOD in leachate, and the microbial yield coefficient (Y) are reported in Table 4. The X_a increased as the influent TCLE concentration increased and/or EBRT decreased (an increase in influent TCLE loading), likely because the biofilm growth was directly related to TCLE elimination capacity. Furthermore, carbon for cell growth could also be from organic compounds dissolved from the coal. The X_a values collected in this work ranged from 1.78 to 4.48 g/L, which appear to be much lower than those reported in the literature *(7)*. This was because the influent VOC concentration of this study was relatively low, which might have caused slow biofilm growth in the TBAB.

The P value significantly increased as EBRT decreased. This was because P linearly depends on the superficial gas flow rate *(19)*. The P value also slightly increased with the increase in influent TCLE concentration. This can be attributed to the fact that more micro-organisms were yielded under a higher TCLE feed, which might have minimized the external

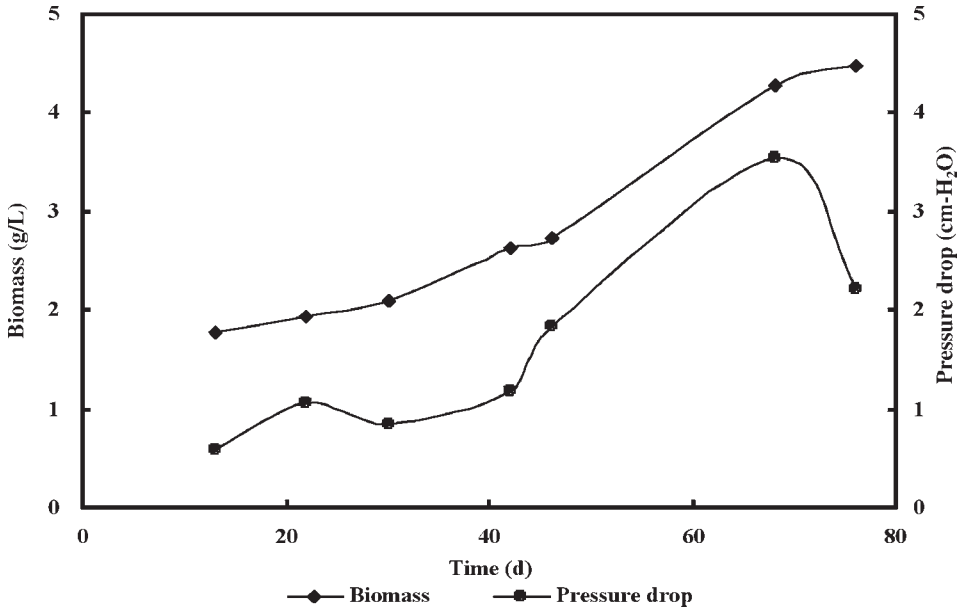

Fig. 4. Time behaviors of attached biofilm mass per unit volume of coal particle (X_a) and pressure drop across the bed (P).

porosity of the coal particles and thus led to a higher pressure drop across the bed. Figure 4 shows the values of X_a and P as a function of operating time. As can be seen, the X_a level increased as the operating time increased. The TBAB was operated about 76 d from Runs 1–7. During this period, the P values were very low and ranged from 0.59 to 3.55 cm H_2O, because of slow biofilm growth.

The leachate production rate was approx 3 L/d. The SCOD of the leachate can be mainly related to dissolved TCLE vapor. With the exception of Run 5, the SCOD of the leachate increased as the influent TCLE concentration increased or EBRT decreased and ranged from 32 to 82 mg/L.

As can be seen in Table 4, the growth yield (Y) was much less than unity, indicating that the fraction of TCLE associated to cells production was usually very small. The influent chemical oxygen demand (COD) loading was in the range 0.04–0.25 kg COD/m^3 d. The resulting Y value ranged from 0.004 to 0.048, with an average of 0.024, which was smaller than the typical value of 0.08 for the removal of benzene, toluene, ethylbenzene, and xylene (BTEX) mixtures by TBAB systems in the COD loading range of 0.45–6.2 kg COD/m^3 d *(6)*.

Figure 5 shows the results of suspended solid (SS) and volatile suspended solid (VSS) in leachate and mass ratio of VSS to SS (η) as a function of the operating time. The VSS of the leachate can be mainly related to sloughed biofilm. As can be seen, the values of SS and VSS in the leachate ranged from 9.06 to 83.18 mg/L and 8.68 to 79.85 mg/L, respectively. The η values were in the range 0.84–0.98, indicating that most of the

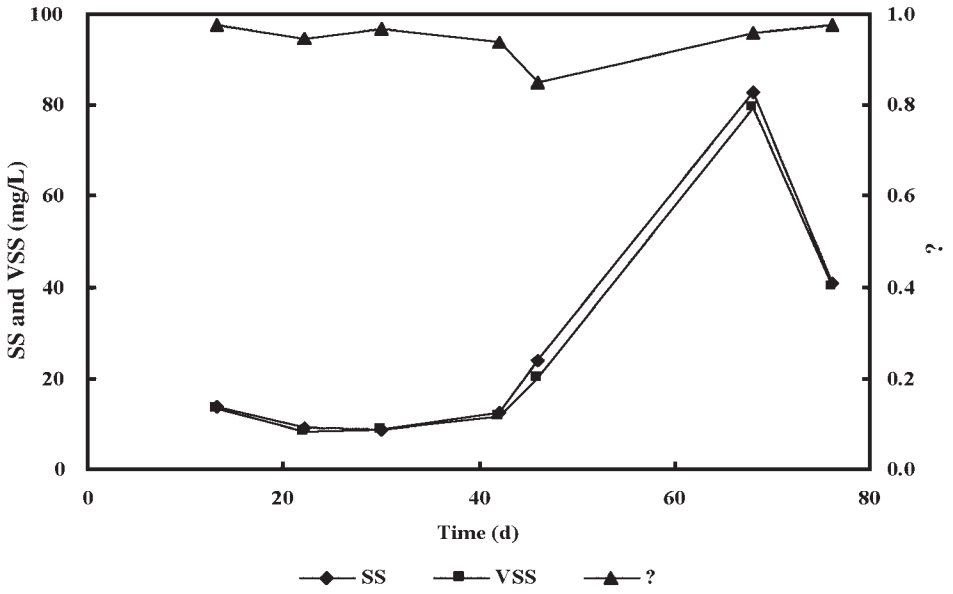

Fig. 5. Time behaviors of suspended solids (SS) and volatile suspended solids (VSS) in leachate and mass ratio of VSS to SS.

Table 5
Carbon Balance Analysis of the Runs

Run no.	Q_aC_i (mg C/min)	Q_aC_e (mg C/min)	Q_aC_c (mg C/min)	αQ_lC_b (mg C/min)	βQ_lC_l (mg C/min)	R (%)
1	0.80	0.00	0.76	0.01	0.02	98.77
2	1.09	0.00	1.05	0.01	0.03	99.45
3	1.64	0.00	1.63	0.01	0.03	102.17
4	3.34	0.00	3.15	0.01	0.03	95.78
5	3.41	0.00	3.32	0.02	0.03	98.88
6	5.81	0.00	5.42	0.08	0.06	95.79
7	5.89	0.00	5.95	0.04	0.05	102.49

SS in the leachate came from sloughed biofilm. The SS and VSS in leachate were relatively higher at a shorter EBRT. This can be attributed to higher fluid shear stress caused by a higher superficial gas flow rate.

The results of the carbon balance listed in Table 5 show that carbon recovery (R) was particularly high (> 95%), indicating the accuracy of test results. Most of the effluent carbon was from CO_2 production (above 99%). The carbon mass rate of the liquid effluent only ranged from 0.02 to 0.06 mg C/min, which was approximately two orders of magnitude less than that of the CO_2 effluent (0.76–5.95 mg C/min). Therefore, it could be concluded that dissolved TCLE and its derivatives in the leachate were present in negligible amounts in the TBAB.

Conclusions

The following conclusions could be drawn from this study:

1. Coal particles appeared to be very efficient for buffering the fluctuations in TCLE concentration.
2. Nearly complete TCLE removal could be achieved for influent carbon loading between 0.98 and 5.88 g/m^3 h, indicating that the TBAB could be efficient for controlling TCLE emission under a low-carbon-loading condition.
3. During the experimentation period, the pressure drops across the bed (P) were very low and ranged from 0.59 to 3.55 cm H_2O, because of slow biofilm growth.
4. Carbon balances showed that high carbon recoveries (R) > 95% were achieved and most of the effluent carbon was from CO_2 production (above 99%). The carbon mass rate of the liquid effluent was approximately two orders of magnitude less than that of the CO_2 effluent, indicating that dissolved TCLE and its derivatives in the leachate were present in negligible amounts in the TBAB.

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References

1. Purdom, P. W. (1980), *Environmental Health*, 2nd ed., Academic, New York.
2. United Nations Environmental Program (April 2002), Montreal Protocol on Substances that Deplete the Ozone Layer. Available at http://www.unep.ch/ozone/Teap-Reports/Teap-Report-April2002-vol2.doc. Accessed June 12, 2003.
3. Corsi, R. L. and Seed, L. (1995), *Environ. Prog.* **14,** 151–158.
4. Ottengraf, S. (1986), in *Biotechnology, Volume 8*, Rehm, H. J. and Reed, G. (eds.), VCH, Weinheim, pp. 425–452.
5. Abumaizar, R. J., Kocher, W., and Smith, E. H. (1998), *J. Hazard. Mater.* **60,** 111–126.
6. Sorial, G., Smith, F., Suidan, M., Pandit, A., Biswas, P., and Brenner, R. (1997), *J. Environ. Eng.* **123,** 530–537.
7. Lu, C., Lin, M., and Chu, W. (2000), *J. Air Waste Manag. Assoc.* **50,** 411–417.
8. Sorial, G., Smith, F., Suidan, M., Pandit, A., Biswas, P., and Brenner, R. (1998), *Water Res.* **32,** 1593–1603.
9. Lu, C., Lin, M. R., and Lin, J. (2001), *J. Hazard. Mater.* **B82,** 233–245.
10. Lu, C., Lin, M. R., and Lin, J. (2000), *Bioresource Technol.* **75,** 35–41.
11. Lu, C., Lin, M. R., and Lin, J. (2001), *Chemosphere* **44,** 173–180.
12. Lu, C., Lin, M. R., and Lin, J. (2001), *Waste Manag. J.* **21,** 489–498.
13. Lu, C., Lin, M. R., Lin, J., and Chang, K. (2001), *J. Biotechnol.* **87,** 123–130.
14. Bouwer, E. J. and McCarty, P. L. (1982), *Environ. Sci. Technol.* **16,** 836–843.
15. Kim, Y., Arp, D. J., and Semprini, L. (2002), *Biotechnol. Bioeng.* **77,** 564–576.
16. American Public Health Association (APHA) (1995), *Standard Methods for the Examination of Water and Wastewater*, 19th ed. Washington DC.
17. Swanson, W. and Loehr, R. (1997), *J. Environ. Eng.* **123,** 538–546.
18. Gaudy, A. and Gaudy, E. (1980), *Microbiology for Environmental Scientists and Engineers*, McGraw–Hill, New York.
19. Crawford, M. (1976), *Air Pollution Control Technology*, McGraw–Hill, New York.