Biotrickling Filtration for Control of Volatile Organic Compounds from Microelectronics Industry

Walter Den[1]; Chihpin Huang[2]; and Chi-Han Li[3]

Abstract: This study investigated the transient and steady-state performance of a bench-scale biotrickling filter for the removal of an organic mixture (acetone, toluene, and trichloroethylene) typically emitted by the microelectronics industry. The microbial consortium consisting of seven bacterial strains that were fully acclimated prior to inoculation onto activated carbon media. Among the seven strains, the *Pseudomonas* and *Sphingomonas* strains appeared to be the major groups degrading toluene (>25 ppmv/h$\cdot 10^8$ cell) and trichloroethylene (>2.3 ppmv/h$\cdot 10^8$ cell), while *Mycobacteria* and *Acetobacteriaceae* strains were the primary decomposers of acetone (>90 ppmv/h$\cdot 10^8$ cell). The column performance was evaluated by examining its responses to the fluctuating influent total hydrocarbon concentrations, which varied from 850 to 2,400 ppmv. Excellent steady-state removal efficiencies greater than 95% were consistently observed, and system recovery was typically within two days after a significant increase in the inlet loading was experienced. The overall mass-transfer rate and the biokinetic constants were determined for each organic component. Mathematical simulations based on these parameters demonstrated that the removal of acetone was kinetically limiting, whereas the removals of toluene and trichloroethylene were at least partially mass-transfer limiting.

DOI: 10.1061/(ASCE)0733-9372(2003)129:7(610)

CE Database subject headings: Filters; Volatile organic chemicals; Air pollution; Kinetics; Industrial wastes.

Introduction

High-volume production of integrated circuits requires a considerable number of precisely controlled processes that are continually and rapidly evolving. In the age of nanotechnology, wafer fabrication and packaging typically require highly repetitive processes involving the use of a wide variety of toxic chemicals and gases (U.S. EPA 1995). Traditionally, much concern was directed toward the occupational health and safety issues, yet the nature of the industry also suggests potential emission of many environmental pollutants. For example, highly volatile organic solvents such as acetone, isopropyl alcohol (IPA), and trichloroethylene (TCE) are frequently used for vapor treatment in both wafer fabrication and printed circuit board applications. Furthermore, a significant portion of the chemicals used in photolithography is considered volatile, such as propylene glycol methyl ether acetate (PGMEA), methyl ethyl ketone, hexamethyldisilane (HMDS), and butyl acetate, particularly when the lithographic processes involve thermal treatment (Wu et al. 2001). Coogan and Jassal (1997) and Wolfrum et al. (1997) reported a mixture of PGMEA [<100 parts per million by volume (ppmv)] and HMDS (<100 ppmv) from a phototrack system during operation, as well as a mixture of acetone (<250 ppmv), methanol (<175 ppmv), and perchloroethylene (PCE) (<6 ppmv) from the solvent cleaning hood. Our previous study in a small-scale wafer fabrication facility also showed that the waste gas contained a mixture of acetone (<800 ppmv), IPA (<50 ppmv), toluene (<20 ppmv), and TCE (<13 ppmv) vapors (Den 2001). The waste emission was characterized by substantial fluctuation in the total hydrocarbon (THC) concentration, a surrogate parameter accounting for all volatile organic compounds (VOCs), due to the cyclical nature of the batched fabrication processes. Therefore, the emission of VOCs from microelectronic fabrication facilities must be sufficiently controlled to comply with the federal and local emission standards for hazardous air pollutants.

While physical or thermal approaches such as carbon adsorption and thermal (catalytic) oxidation have proven successful in removing VOCs from waste gases, biological treatment processes are generally regarded as a more cost-effective technology. This has led to a wealth of literature reports demonstrating the feasibility of using biological filtration as the VOC control strategy for a variety of industrial emissions, such as boat manufacturing (Lackey et al. 1998), petrochemical processing (van Groenestijn and Lake 1999), painting operations (Kiared et al. 1996; Kim et al. 2000), and various remediation off-gases (Leson and Winer 1991; Wright et al. 1997). The large-volume, low-VOC concentration characteristics of waste emissions from the microelectronics industry also make the biological filtration process an attractive candidate for VOC emission control. In the past, biological filters simply comprised packed beds of naturally bioactive materials such as soil and compost, but they proved to be short lived because of the lack of control over the packing medium and microbial community. More recently, synthetic packing media were used to maintain the long-term structural integrity of packed beds,

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Note. Associate Editor: Bruce Ernest Logan. Discussion open until December 1, 2003. Separate discussions must be submitted for individual papers. To extend the closing date by one month, a written request must be filed with the ASCE Managing Editor. The manuscript for this paper was submitted for review and possible publication on September 18, 2001; approved on August 26, 2002. This paper is part of the ***Journal of Environmental Engineering***, Vol. 129, No. 7, July 1, 2003. ©ASCE, ISSN 0733-9372/2003/7-610–619/$18.00.

and to improve the air distribution through the filters. The coupling of activated carbon and biofilm, namely, bioactive carbon, has also shown mutually beneficial effects by the ''bioregeneration'' phenomenon (Speitel et al. 1987; Kim and Pirbazari 1989). Further, development of biotrickling filters, which involve a continuously or intermittently flowing aqueous phase, provides even better control over environmental conditions such as nutrient supply, pH neutralization, and purging of toxic degradation metabolites (Fortin and Deshusses 1999).

Despite the progress made in improving biological filtration technologies, the most critical element dictating the biofilter or biotrickling filter performance is the selection and maintenance of proper microbial activity over a long-term basis, particularly for treatment of VOC waste emission with variable loading conditions. The lack of control over the microbial element often gives rise to problems such as a long start-up period, low microbial activity, and low tolerance of concentration fluctuations. All these issues are potential reasons for inadequate performance that cannot be easily resolved after commencement of system operations. In view of these problems, a number of studies have demonstrated the used of well-structured mixed bacterial consortium for treatment of organic waste streams, particularly when one or more toxic organic compounds are present (Bitzi et al. 1991; Quinlan et al. 1999). Maier (1989) also described microbial strategies for degradation of mixed substrates, and subsequently the need of a multiple bacterial culture for more efficient removal. The objective of this work, therefore, was to evaluate the performance of a biotrickling filter under variable loading conditions, and to demonstrate the favorable effects of microbial preoptimization prior to inoculation for column experiments. The concentration ranges of the VOCs (acetone, TCE, and toluene) were similar to the actual patterns of waste gas emitted from microelectronics fabrication facilities. This type of mixture manifests a rather complex multiple-component system with respect to both biodegradability and water solubility. Therefore, kinetic analyses were also conducted in conjunction with a simple mathematical model to examine the process kinetics of VOCs in a biotrickling filter.

Materials and Methods

Microbial Culture

Activated sludge samples obtained from an industrial wastewater treatment facility (Hsinchu, Taiwan) were allowed to settle for 1 h, and the supernatant was collected for enrichment of microbial culture. Initial acclimation was proceeded by feeding a vapor mixture of filtered air, acetone (300 ppmv), and toluene (25 ppmv) into a cell fermentor containing 300 mL of culture in a mineral medium (KH_2PO_4 8.5 mg; K_2HPO_4 33.4 mg; Na_2HPO_4 17.4 mg; NH_4Cl 1.7 mg; $MgSO_4$ 11 mg; with 5.0 g tryptone and 2.5 g yeast in 0.992 L of distilled water). After 24 hours, the vapor concentrations of acetone and toluene were increased to 600 and 50 ppmv, respectively, along with an intermittent supply of TCE (~5 ppmv) for 30 min in each 4-h interval. After 36 hours of acclimation, 1-mL culture samples at three different dilution levels were transferred separately onto plate count agar and potato dextrose agar (Difco), followed by incubation at 30°C for 36 hours. After a series of culture enrichment and isolation procedures, the microbial cultures were purified, and the growth pattern of each strain was recorded. These purified strains were then subjected to identification and biodegradation experiments.

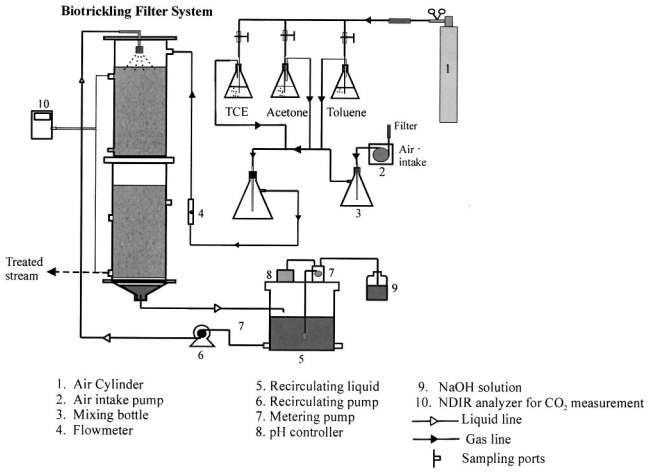

Fig. 1. Experimental setup for biotrickling filter system

Biotrickling Filter Configuration

A laboratory-scale biotrickling filter was constructed to investigate the transient and steady-state removal of a synthetic vapor mixture of acetone, toluene, and TCE. The biotrickling filter schematized in Fig. 1 was a two-stage acrylic bioreactor (internal diameter, 7 cm; height, 30 cm each stage) designed to enhance liquid distribution in the packed bed. The VOCs, independently vaporized by sparging filtered air into the liquid solvents through high-precision needle valves, were mixed with the bulk air and entered the biotrickling filter from the top of the column. Concentrations of the VOCs were controlled primarily by the air sparging rate, with the bulk air volume as a secondary method. The column was packed to a depth of 25 cm in each stage with granular activated carbon (GAC, type BLP, Calgon Carbon Corporation, Pittsburgh) having a mesh size of 6×12.

The recirculating liquid was uniformly distributed across the top of the filter bed through a spray nozzle at a rate of 1.5 L/min. The liquid drain was then circulated to a 40-L tank equipped with a mechanical stirrer and a pH controller. Fresh mineral medium (KH_2PO_4 500 mg/L;K_2HPO_4 500 mg/L;NH_4Cl 50 mg/L) was added regularly to the circulating liquid for replenishment of inorganic nutrients to the microorganisms.

Biodegradation Studies

Shake-flask experiments were conducted to characterize the biodegradation capability of the isolated bacterial species for the target VOCs. Pure culture (150 mL) (diluted to a starting cell density of ~100 cfu/ml) was transferred to 250-mL Erlenmeyer flasks sealed with an air sampling device and thoroughly stirred. Appropriate quantities of reagent-grade acetone, toluene, and TCE were added to the flasks until reaching desired headspace concentrations using the following equilibrium relationship:

$$C_L = C_g\left(\frac{1}{H_c} + \frac{V_f}{V_L} - 1\right) \quad (1)$$

where C_g and C_L=gas and liquid concentration, respectively; V_L and V_f=volumes of the liquid in the flask and of the flask itself; and H_c=Henry's law constants for the VOCs. Each set of experiments was performed in duplicate in 30°C, along with a flask containing sterilized liquid to serve as the blank control. Headspace sampling using valved syringes occurred every 30 min for

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Table 1. Loading Conditions for Biotrickling Filter

Phase	Days	Inlet total hydrocarbon concentration (ppmv)	Inlet acetone concentration (ppmv)	Inlet toluene concentration (ppmv)	Inlet trichloroethylene concentration (ppmv)	Empty bed contact time (s)
1	0–31	850	220	50	10	155
2	32–43	1,250	325	75	15	155
3	43–53	2,400	470	200	40	155
4	53–67	1,750	345	145	30	155
5	67–77	2,400	470	200	40	310
6	77–84	850	220	50	10	155

the first 4 hours, and every 4 hours afterward. The biodegradability of each component of the VOC mixture by a pure culture was evaluated using Eq. (2)

$$R_{\mathrm{VOC}}=\frac{\text{hourly disappearance of VOC concentration}}{10^8 \text{ cell}} \tag{2}$$

Biotrickling Filter Performance Studies

A total of 0.8 kg of mixed bacterial consortium (equal % by weight of each purified strain) was inoculated onto 1.375 kg GAC prior to the column operation. The GAC was thoroughly washed with nitric acid (0.1 M) to remove fine particles and to adjust its pH to neutral range. During the experiments, the ambient temperature was within 28±2°C, and the pH was maintained in the range of 6.5 to 7.5 by the addition of 1 M NaOH in the circulation tank. In order to systematically evaluate the performance of the biotrickling filter, the column operation was divided into three operating stages. These include (1) a start-up period with lower range of THC inlet concentration; (2) fluctuating inlet THC concentrations; and (3) change of empty bed contact time (EBCT). Detailed experimental conditions are specified in Table 1. During the column study, gaseous samples were collected daily using Teflon sampling bags (Type L, Alltech Inc., Deerfield, Ill.) from the inlet, midcolumn, and outlet of the biotrickling filter.

Kinetic Analysis

In all gas-phase trickle-bed reactors, two limiting factors must be investigated, namely, the gas-liquid mass transfer of VOCs, and the degradation rate of VOCs within the biofilm. For this reason, a mathematical model previously developed by Barton et al. (1998) was employed in this work to evaluate the roles of Monod-type biodegradation and mass-transfer rate in biotrickling filters. The model consists of two fundamental equations

$$\frac{dY^g}{dz}=-\frac{K_l a}{H_c}(Y^g-Y^l)\left(\frac{SRT}{G}\right) \tag{3}$$

and

$$\frac{dY^l}{dz}=\frac{S}{L}\left[K_l a(Y^g-Y^l)-XH_c a\frac{V_m Y^l}{K_s+Y^l}\right] \tag{4}$$

where Y^g and Y^l=molar fraction of VOCs in gas and liquid phases, respectively; $K_l a$ and H_c=liquid mass-transfer resistance and Henry's law constant; and V_m and K_s=Monod kinetic parameters. In principal, Eq. (3) describes the rate of VOC disappearance as a function of mass transfer from the gaseous to the liquid phase, and Eq. (4) describes the rate of removal in the liquid phase due to biofilm degradation. The system of equations is valid for steady-state conditions, and is restricted to ideal gases, constant temperature, free of mixing, and uniform packing. The model further assumes that radial effects are negligible, and that biofilm characteristics are uniform throughout the column. These assumptions imply a nongrowth scenario with respect to the biofilm thickness and density within a finite time period, and therefore the VOC and O_2 concentration profiles in the biofilm remain essentially constant.

The biokinetic parameters in Eq. (4) can be estimated by adopting a Monod-based, plug-flow type equation derived by Hirai et al. (1990) for an immobilized-cell biofilter

$$\frac{dC}{dz}=\left(\frac{-V_m C}{K_s+C}\right)\frac{\alpha}{Z\times SV} \tag{5}$$

where $SV\,(\mathrm{h}^{-1})$=space velocity; and α (kg dry particle/g VOC) =conversion factor. By integration of Eq. (5) using the boundary conditions of $C(z=0)=C_0$ and $C(z=Z)=C_e$, a Lineweaver-Burke form can be obtained

$$\frac{1}{R_r}=\frac{K_s}{V_m}\frac{1}{C_{\ln}}+\frac{1}{V_m} \tag{6}$$

where

$$R_r=\left[\frac{\alpha}{SV(C_0-C_e)}\right]^{-1} \quad \text{and} \quad C_{\ln}=\frac{C_0-C_e}{\ln(C_0/C_e)} \tag{7}$$

In Eqs. (6) and (7), R_r (g VOC/h/kg dry particle)=removal rate; C_0 and C_e (both in ppmv)=gas-phase influent and effluent VOC concentrations; V_m (g VOC/h/kg dry particle) and K_s (ppmv)=maximum removal rate and saturation constant, respectively. The Monod constants can then be determined from the linear relationship between $1/R_r$ and $1/C_{\ln}$. This method has also been successfully applied to evaluate the biokinetic parameters in other biofilter studies (Chung et al. 1996; Kim et al. 1998; Yani et al. 1998).

The effect of gas/liquid mass transfer can be evaluated by determination of the liquid mass-transfer coefficient $K_l a\,(\mathrm{h}^{-1})$. This can be achieved by employing a similar technique proposed by Barton et al. (1998) based on the following mathematical relationship:

$$\ln(Y^g)=K_l a\frac{Z}{G}\frac{SRT}{H_c}+C_1 \tag{8}$$

where Z (m) and $G\,(\mathrm{m}^3/\mathrm{h})$=packing depth and gas flow rate; $S\,(\mathrm{m}^2)$=column cross-sectional area; T (K)=operating temperature; $R\,(\mathrm{atm\cdot m^3/mol\cdot K})$=gas constant; and C_1=arbitrary constant. The slope of a linear plot between $\ln(Y^g)$ and $(1/G)$ yields a value from which $K_l a$ can be determined.

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Table 2. Characterization of Enriched Microorganisms

Number	Identification	G(+) or G(−)	Substrate biodegradability R[a]		
			Acetone only	Toluene only	Trichloroethylene with toluene
B1	*Pseudomonas*	G(−)	64	46	6.2
B2	*Pseudomonas*	G(−)	62	37	4.2
B3	*Pseudomonas*	G(−)	93	62	7.2
B4	*Sphingomonas*	G(−)	42	24	2.3
B5	*Bacillus spp.*	G(+)	22	14	N
B6	*Acetobacteriaceae*	G(−)	90	N	N
B7	*Mycobacteria*	G(+)	99	N	N
F1	Unknown fungi[b]	—	Y	Y	Y
F2	Unknown fungi[b]	—	Y	Y	N

Note: N indicates "no significant biodegradation." $R<0.5$ was considered nonbiodegradable because a small portion of the substrate may be lost due to adsorption onto cells rather than biodegradation.

[a]R=substrate consumption (ppmv) per hour per 10^8 cells [Eq. (1)]. Data were taken from the initial 8 h of degradation.

[b]Fungi species were observed but were not isolated, and their biodegradabilities were not quantified.

Analytical Methods

The concentrations of acetone, toluene, and TCE were determined by a Shimadzu GC-14B gas chromatograph (Shimadzu Analytical Instrument Co., Kyoto, Japan) equipped with a flame ionization detector and a 30-m, AT-1 fused silica capillary column (Alltech Associates, Inc., Deerfield, Ill.). Due to the low effluent concentrations of these compounds, a thermal desorption unit (Tracer-1000, Quadrex, Taiwan) equipped with multiple switch valves for sample trapping and injection was installed to enhance the sensitivity of the instrument. The oven temperature was programmed with the following conditions: 50°C for 5 min, 50–150°C at 10°C/min, and 150°C for 2 min. The injector and detector temperatures were set at 200 and 300°C, respectively. To quantify the THC concentration, a 15-m, deactivated fused silica capillary column was used in place of the AT-1 column. Standard methane gases (100 and 1,000 ppmv in N_2, Scott Specialty Gases, Plumsteadville, Penn.) were used to establish standard calibration for the THC concentration. Therefore, all THC concentrations are expressed as CH_4 in this study. Carbon dioxide concentration was monitored at the inlet and outlet ends of the column using a nondispersive infrared analyzer (Telaire 1050, Telaire System Inc., Goleta, Calif.). The yield of CO_2 could then be determined by subtracting the background level (inlet) from the outlet concentration. The instrument was capable of measuring up to 2,000 ppmv of CO_2, with an analytical accuracy within 5% of reading. This monitoring procedure allows for estimating the extent of organic carbon mineralization in a continuous mode.

The isolated bacterial strains were identified by following the standard Biolog procedure, with positive identification based on similarity between the "fingerprint" pattern of the strain and the MicroLog 1 database. Those that could not be positively identified by the Biolog procedure were then identified using the conventional taxonomy characterization. Additionally, to correlate the column performance with the microbial activity, cell enumeration was periodically performed. Approximately 10 cell-laden GAC media were withdrawn from the upper and lower portions of the packed bed and preserved in saline solution, and quantification was determined by adopting the "plate dilution frequency" method described by Harris and Sommers (1968). Visual observation of the biofilm was facilitated by using scanning electron microscopy (SEM) following the preparation procedure described by Pirbazari et al. (1990).

Results and Discussion

Microbial Culture Characteristics and Volatile Organic Compound Biodegradability

After a 5-day acclimation period, the original culture was enriched with acetone and toluene, and subsequently isolated by the serial transfer technique under aseptic conditions. A total of nine microbial species (Table 2) were successfully isolated, including seven bacterial strains (labeled B1–B7) and two fungal strains (F1,F2). Considering that fungal overgrowth may be detrimental to bacterial growth, and that it may easily clog the porous space during column operation, the fungal species were excluded from this study.

Fig. 2 shows the growth curves of B1–B7 with acetone and toluene. Similar growth patterns were observed between the three *Pseudomonas* strains (B1–B3), the *Sphingomonas* strain (B4), and the *Mycobacterium* strain (B7). These bacteria all exhibited an exponential growth phase between 4 and 24 hours, followed by a stationary phase for the next three days before decaying. In contrast, the *Bacillus* strain (B5) was characterized by rapid initial

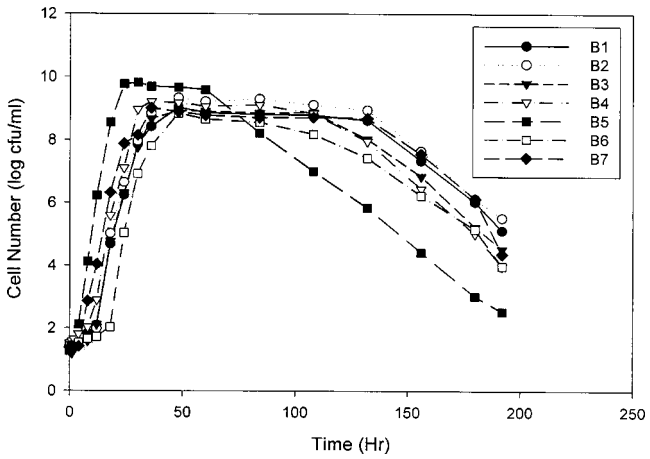

Fig. 2. Growth patterns of bacterial strains (B1–B7) comprising mixed consortium on acetone and toluene

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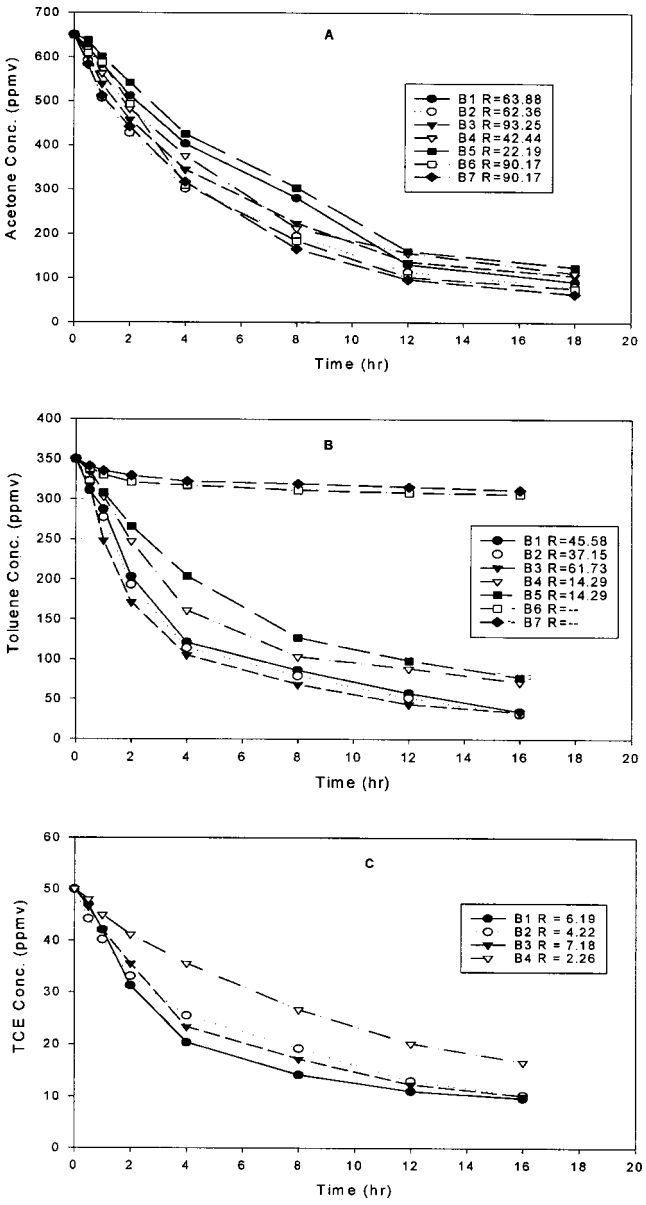

Fig. 3. Biodegradability of (A) acetone, (B) toluene, and (C) trichloroethylene, by bacterial strains comprising mixed consortium

growth but a substantially shorter stationary phase, whereas the *Acetobacteriaceae* strain (B6) required an extended lag phase before experiencing growth.

To examine the biodegradability of the target VOCs by each bacterial strain, the pure cultures were exposed to a mixture of acetone, toluene, and/or TCE. As shown in Fig. 3, all seven strains were capable of degrading acetone, with B7 showing the highest degradability (99.2 ppm/10^8 cell/h) and B5 the lowest (22.2 ppm/10^8 cell/h). As for toluene, all of the strains except B6 and B7 showed various degrees of biodegradation (14.3–61.7 ppm/10^8 cell/h). The slight reduction in toluene concentration in B6 and B7 cultures was most probably due to adsorption rather than biodegradation.

Trichloroethylene is known to be biodegraded with significantly higher rates by cometabolism than by catabolism under aerobic conditions. This is manifested by the observation that TCE can be efficiently degraded by a number of mono- or dioxygenases induced by various alkane and aromatic compounds, but is relatively insensitive to attack by hydrolytic dehalogenases via substitutive dehalogenation pathways (Hanson and Brusseau 1994; Fetzner 1998). These TCE cometabolizing oxygenases, which generally exhibit low substrate specificity, use exogenous carbon as growth substrate and electron donor to supply NAD(P)H for the oxygenase reactions. This oxidative dehalogenation mechanism is known to transform TCE to its epoxide (i.e., TCE epoxide), an unstable product that subsequently undergoes isomerization or hydrolysis to form intermediates such as glyoxylic acid, dichloroacetic acid, or formic acid. Furthermore, when toluene was used as the inducer, a number of bacterial strains belonging to the genus *Pseudomonas* have been shown to express the mono- and dioxygenases capable of TCE degradation (Nelson et al. 1987; Wackett and Gibson 1988; Shields et al. 1989; Winter et al. 1989). In the present study, when toluene of 150 ppmv served as the primary substrate, all three *Pseudomonas* species (B1–B3) showed significant TCE degrading capability. The *Sphingomonas* species (B4) was also capable of TCE biodegradation, although the degradation rate (2.3 ppm/10^8 cell/h) was considerably lower than those observed with the *Pseudomonas* strains. None of these bacteria was capable of degrading TCE without the copresence of toluene, showing that the TCE degradation was predominantly due to toluene-induced cometabolism.

In comparison to other design aspects of gas-phase biofiltration or biotrickling filtration, relatively little attention has been directed toward the microbial structure of the biofilm during system operation. Yet the biochemical processes and the metabolic interactions among microflora communities exposed to a multicomponent substrate (VOCs) are decisively important to the success or failure of a long-term biofilm treatment process. For the microbial consortium constructed in this study, strains B6 and B7 were clearly responsible for acetone biodegradation because they did not utilize toluene or TCE as growth substrate. It should also be noted that the toluene degraders (B1–B5) were also acetone degraders, with noticeably higher degradation rate of acetone over toluene. These characteristics indeed present an ambiguity as to whether competitive inhibition or single-species dominance will occur when the consortium is exposed to the multicomponent VOC mixture. More complex situations, such as the lateral gene transfer phenomenon between related or unrelated species, may also occur due to the close cell proximity (Atlas and Unterman 1999). The occurrence of LGT is thought to greatly contribute to the extraordinary variation of bacteria with reference to their metabolic properties and cellular structures by means of horizontal gene transfer. This phenomenon occurs by transformation (uptake of naked DNA from the environment) or conjugation (physical contact between donor and recipient) (Ochman et al. 2000); therefore it would not be surprising if natural genetic exchange even between very distantly related species were to occur in biofilm systems. However, these situations involving genetic exchange mechanisms remain to be verified in the actual operation of biofilters.

The information gained from these fundamental growth pattern and biodegradability studies should not be overlooked, because the bacterial growth in biotrickling filter operation is preferably near the end of the exponential growth phase or in early stationary phase. This is an important aspect not only for sustaining an active biofilm, but also for preventing the clogging problem arising from cell overgrowth. Consequently, the net rate of cell growth in the system should approach zero by balancing the rate of growth with the rate of endogenous decay. Combining the use of this equilibrium with the steady-state material balance for a plug-flow reactor, the mean retention time of waste gases (i.e., the

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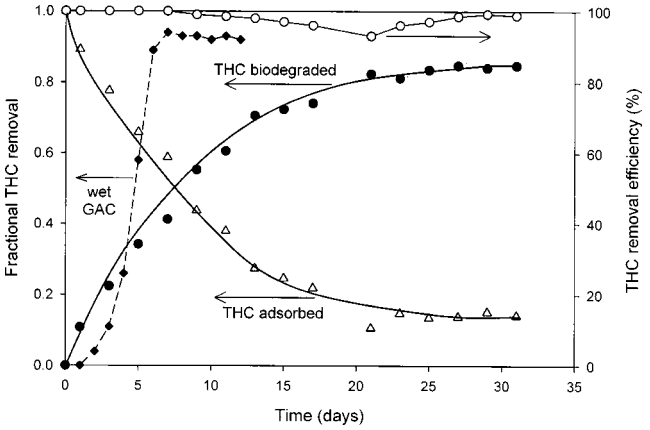

Fig. 4. Total hydrocarbon removal profile and corresponding fractional removals by adsorption and biodegradation during start-up period (Phase 1, nominal inlet total hydrocarbon concentration 850 ppmv, empty bed contact time 155 s). Adsorption breakthrough profile of nonbioactive granular activated carbon (empty bed contact time 310 s) is also shown.

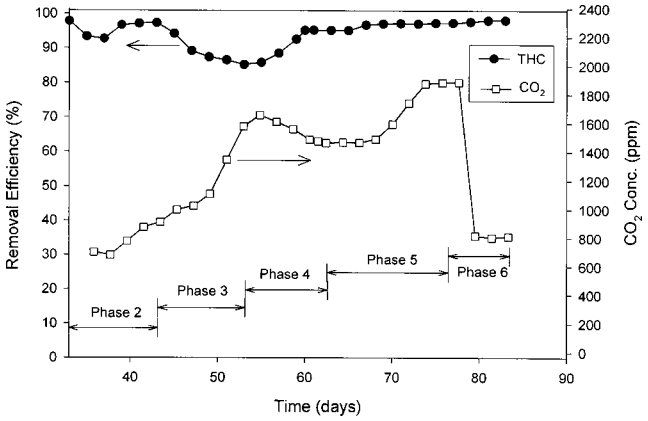

Fig. 5. Removal profiles and corresponding carbon dioxide evolution under fluctuating total hydrocarbon loading conditions (loading conditions are specified in Table 1)

EBCT) in biotrickling filters could be approximated based on knowledge of the bacterial growth pattern. In this work, it was estimated that a retention time of 3 min would yield cell numbers on the order of 10^8 cells/mL, corresponding to the values in the proximity of the stationary phase as shown in Fig. 2. This result provides a preliminary estimate for the appropriate retention time in a biotrickling filter, and an EBCT of 2.5 min was chosen accordingly for the column operation in this study.

System Start-up Performance

Fig. 4 shows the profiles of THC removal efficiency and the corresponding THC fractional removals by adsorption and biodegradation for the biotrickling filter during the initial phase (Phases 1 in Table 1). The starting nominal THC concentration was 850 ppmv with an EBCT of 155 s. The figure also includes the adsorption breakthrough profile of the nonbioactive GAC under ''wetted'' conditions (i.e., with water spraying but no microbial inoculation). It can be observed from the THC removal efficiency profile that no breakthrough occurred until the tenth day of column operation, and that the removal efficiency never decreased below 90%. This breakthrough-free period was significantly extended compared to the nonbioactive adsorption profile under the same influent concentrations but with only half the EBCT. The marked differences in the breakthrough periods were clearly attributable to the bioactive nature of the carbon. Furthermore, the relative contribution to the overall THC removal by either adsorption or biodegradation indicated that the microbial consortium was yet to be fully acclimated during the initial 20 days of operation. During this period, carbon adsorption played a prominent role in the THC removal, but the adsorption capacity was gradually exhausted and breakthrough eventually occurred. As the CO_2 evolution gradually reached a steady-state plateau after 20 days, biodegradation of the VOCs became primarily responsible for the THC removal. These removal patterns were established assuming that the accumulation of metabolic intermediates was negligible, which appeared to be a legitimate postulate considering the near-unity stoichiometric relationship between the CO_2 produced and the THC removed. This figure clearly reveals the change of roles between adsorption and biodegradation, as well as the two mechanisms complementarity to each other with respect to maintaining high THC removal efficiency during the column start-up period.

System Performance under Variable Loading Conditions

To evaluate the biotrickling filter performance under fluctuating loading conditions, step changes of influent THC concentration or EBCT were conducted for the next 50 days (Phases 2–6) of column operation. It should be mentioned that the relative proportions of the VOC components in the mixture for each loading condition (Table 1) were designed to project the acetone-predominant characteristics of the waste gas, and to sustain toluene-induced cometabolism of TCE. Therefore, the molar ratio of acetone to THC was maintained within the range of 0.5–0.6, and the concentration ratio of toluene to TCE was close to 5. The latter ratio was a critical criterion that provides conditions where cometabolism is stimulated, yet competitive inhibition must be prevented. The results from the biodegradability studies and those reported by Cox et al. (1998) suggested that the appropriate range of the toluene-to-TCE ratio was between 3 and 5. Under these circumstances, system performance with reference to THC removal could be evaluated with minimal variation caused by the potential interaction between the VOC components.

As shown in Fig. 5, a THC step increase from 850 to 1,250 ppmv led to a marginal and temporary reduction in removal efficiency to 92%; the system quickly restored its equilibrium in the vicinity of 96% within two days. Further increase in the influent concentration to 2,400 ppmv (Phase 3) yielded a more significant efficiency reduction, reaching a valley of only 85% THC removal efficiency. However, it was observed that the CO_2 evolution continued to rise despite the reductions in removal efficiency. This implies that microbial inhibition due to substrate toxicity was not a factor at these concentration levels, and that the microbial consortium was continuously adjusting to the loading conditions. As a result, a lag period was consistently observed before the removal efficiency could be returned to its previous level.

To expedite recovery of removal efficiency from Phase 3, two strategic changes were attempted: lowering the THC loading to 1,750 ppmv (Phase 4), followed by extending the EBCT to 310 s (Phase 5). Both strategies were aimed at reducing the influent loading in terms of the total mass of VOCs entering the reactor.

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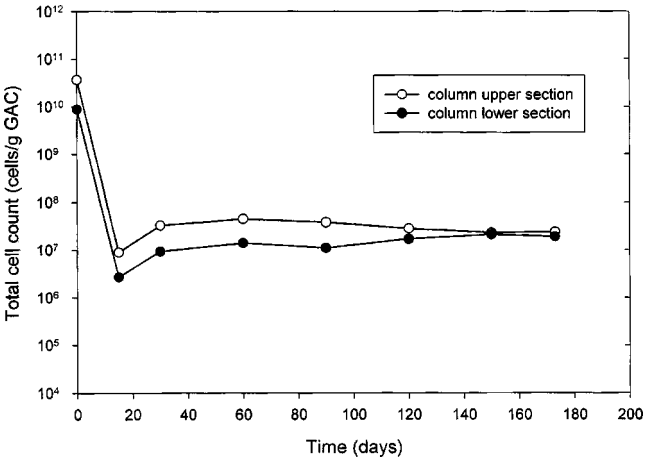

Fig. 6. Microbial enumeration for bioparticle samples taken from upper and lower sections of biotrickling filter

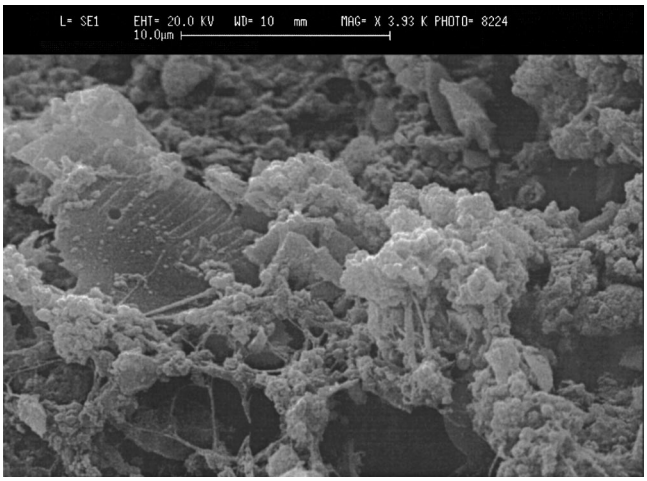

Fig. 7. Scanning electron microscope image showing matured granular activated carbon biofilm matrix of cells, exopolymers, and debris of decayed cells

As a result, gradual efficiency recovery was achieved (~94%) after five days and remained steady afterward. At this juncture (day 63), the inlet concentration was raised back to 2,400 ppmv, whereas the gas flow rate was reduced to extend the EBCT. This movement led to an insignificant change in the removal efficiency, but the CO_2 concentration drastically increased in response to the rise of THC concentration. These results confirmed that the high influent THC concentration (i.e., 2,400 ppmv) was not inhibitory to biofilm degradation, but a threshold limit of its mass removal may have been reached when the high influent concentration was combined with high flow rates (as in Phase 3). Similar lag phases were again observed as those discussed earlier, suggesting that a distinct phase delay between the extent of THC reduction and CO_2 production occurred when the loading conditions were altered, most probably due to the time needed for microbial adaptation to the new loading conditions.

The microbial viability was periodically monitored during the column operation by performing cell enumeration for representative GAC media located on the upper and lower portions of the column (see Fig. 1). As illustrated in Fig. 6, cell enumeration for samples taken at 2 hours after inoculation showed initial cell counts on the order of 10^{10}/g of GAC. After 15 days of operation, a drastic decrease in cell counts by well over three orders of magnitude was observed for both sampling locations. Considering that the system was operated under nutrient-rich conditions (C/N ≈4), an overseeding effect where the ''excess'' cells that did not attach well to the carbon surfaces were washed out by the flowing liquid can be reasonably hypothesized. Similar observations were also made in other biotrickling filter studies (Diks et al. 1994; Weber and Hartmans 1996) with lower superficial liquid velocities than that used in the present study (23.4 $m^3/m^2 \cdot h$). After this point, a slight growth of cell counts was obtained on the 30th day of operation and it seemed to stabilize thereafter in the order of 10^7 cells/g GAC. Note that the cell counts in the upper section of the column were consistently greater than those in the lower section, albeit the differences were only marginal, because of the higher VOC concentrations exposed in the column's upper section. The dry weights of volatile suspended solid (VSS) determined gravimetrically were in the range of 0.1–0.2 g VSS/g GAC. Interestingly, this result implies that the viable cells obtained from the enumeration roughly comprised only 2–4% of the VSS in the biofilm. The remaining solid material observed from SEM images (Fig. 7) mainly included exopolymers (polysaccharides and proteins), decayed cells, and macromolecule residues of the inorganic nutrients. Few literature sources are available for characterization of biofilm composition in a predominantly gas-phase reactor, but the percentage of viable cells compares unfavorably to those (12–33%) reported in water treatment applications (Lazarova and Manen 1995; Lazarova et al. 1998). The relatively higher percentage of exopolymeric matrix might have been excreted by the bacterial cells to promote more efficient cell adhesion onto solid surfaces under the strong abrasive conditions generated by the continuous liquid flow.

The long start-up time has always been a major concern for biofilm reactors due to not only the acclimation period, but also the natural selection of competent microbial cultures. In fact, the latter process often presents a greater obstacle because the density of competent cultures may never develop sufficiently for pollutants containing recalcitrant VOC(s), thus limiting the reactor performance. This study demonstrates that the start-up time can be shortened considerably by prestrengthening the selected bacterial consortium, and that the microbial activity could be easily maintained during column operation. It should also be mentioned that typical problems associated with filter clogging were never observed during the entire course of the study, a result that can be substantiated by the stable cell counts shown in Fig. 6.

Column Removal Kinetics

In this study, the three components in the VOC mixture possess vastly different characteristics with respect to their solubility, volatility, and biodegradability. Therefore, it is anticipated that different mechanisms may be responsible for their removal capacities.

The biokinetic constants determined using the Lineweaver-Burke plot from Eq. (6) are summarized in Table 3. Excellent correlation coefficients (>0.98) were obtained from these plots, manifesting the suitability of Monod-type kinetics in this study. The maximum removal rate constants (V_m) for acetone, toluene, and TCE were 0.23, 0.19, and 0.06 g VOC/h/kg dry particle, respectively, whereas the corresponding saturation constants were 116, 110, and 78 ppmv.

The overall liquid mass-transfer coefficient was estimated by applying Eq. (8) under the assumption that all VOCs in the liquid

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Table 3. Biokinetic and Mass-Transfer Rate Properties of Target Volatile Organic Compounds

Volatile organic compound	Biokinetics[a]		Henry's law constant H_c[b] (atm·m^3/mol)	Overall liquid mass-transfer rate coefficient K_la[c] (h^{-1})
	Maximum removal rate coefficient V_m (g/h/kg dry particle)	Saturation constant K_s (ppmv)		
Acetone	0.23	116	3.97×10^{-5}	28
Toluene	0.19	110	6.64×10^{-3}	32
Trichloroethylene	0.06	78	8.92×10^{-3}	17

[a]Experimentally determined using Eqs. (3) and (4).

[b]Data from Mackey and Shui (1981).

[c]Experimentally determined using Eq. (5).

phase are instantly degraded (i.e., the mass-transfer limiting condition). The estimated values of K_la for acetone, toluene, and TCE were 28, 32, and 17 h^{-1}, respectively. These experimental results appear to be on the higher ends of the spectra as compared to those previously reported (Roberts et al. 1985; Pederson and Arvin 1997). Among the possible causes for the deviation is the significantly higher liquid-to-gas volumetric flow ratio used in the present study. However, considering the fact that the K_la value is highly case specific under different operating conditions, the exact cause for the differences remains inconclusive and is beyond the scope of this study.

In order to investigate whether the removal of the VOCs is kinetically or mass-transfer limited, Eqs. (3) and (4) were solved numerically by the Euler explicit scheme with a step size of $Z/20$. Model simulation profiles were then generated using the parametric values given in Tables 3 and 4. As shown in Fig. 8, the removal profiles with respect to the column depth were simulated for acetone, toluene, and TCE. For each VOC, the simulation was performed by varying the maximum removal rate coefficient (V_m), using the value determined experimentally as the reference (marked in bold in Fig. 8). Under these conditions, acetone appeared to be the most biokinetically sensitive, indicating that the removal of acetone was primarily reaction limiting. On the other spectrum, the removal profiles of TCE were relatively independent of V_m; an increase of two orders of magnitude in V_m only marginally improved the TCE removal efficiency. This result strongly suggests that the removal of TCE was mass-transfer limited. In comparison, the simulated profiles for toluene showed that the removal was somewhat sensitive to the V_m variation, indicating that its removal was partially limited by mass transfer. These simulation studies demonstrate that the importance of identifying the limiting factors in biotrickling filters in order to achieve the required removal efficiency for regulatory compliance. For instance, acetone, as the dominant VOC in this study, was both kinetically and mass-transfer favorable for removal in the biotrickling filter, and thus the system remained highly efficient in THC removal. However, when the dominant pollutant is either highly mass-transfer resistant (e.g., high H_c or low K_la) or biologically recalcitrant, then appropriate actions must be implemented to improve the overall removal efficiency.

Conclusions

The transient and steady-state performance of a bench-scale biotrickling filter for remediation of organic waste gas from a typical microelectronics facility was evaluated. The waste gas mixture contained acetone, toluene, and TCE, whose concentration was measured as THC concentration. The microbial consortium consisting of seven bacterial strains was fully acclimated prior to inoculation on the packing material, and the bacterial individual growth patterns and biodegradation of each compound were characterized. The pseudomonads were highly efficient for degradation of all three VOCs, and along with *Sphingomonas* species were primarily responsible for toluene and TCE biodegradation. In contrast, *Acetobacteriaceae* and *Mycobacteria* strains specialized in degradation of acetone (>90 ppmv/h·10^8 cell).

The system operation under fluctuating THC concentration (850–2,400 ppmv) was investigated. Efficiency recovery, which reflects the column's transient response, typically occurred within two days after a step increase of THC concentration was experienced. However, a threshold capacity for the column appeared to be reached at a THC concentration of 2,400 ppmv and an EBCT of 155 s, although no evidence of any inhibitory effect was observed since the stoichiometric ratio of THC to CO_2 (mineralization) approached unity. When the overall inlet loading was reduced, the steady-state removal efficiency gradually recovered it previous level of greater than 95%. Furthermore, mathematical

Table 4. Entry Values of Operating Parameters Used in Model Simulation

Parameter	Unit	Value
Z (column length)	m	0.05
R (gas constant)	atm·m^3/mol·K	8.21×10^{-5}
S (column cross-sectional area)	m^2	0.00385
a (volumetric surface area of granular activated carbon)	m^2/m^3	150
G (gas flow rate)	m^3/h	0.045
L (liquid flow rate)	m^3/h	0.070
X (areal biofilm density)	g/m^2	100
Y_0^g (influent gas concentration)	—	5.0×10^{-4} acetone
		2.0×10^{-4} toluene
		4.0×10^{-5} trichloroethylene

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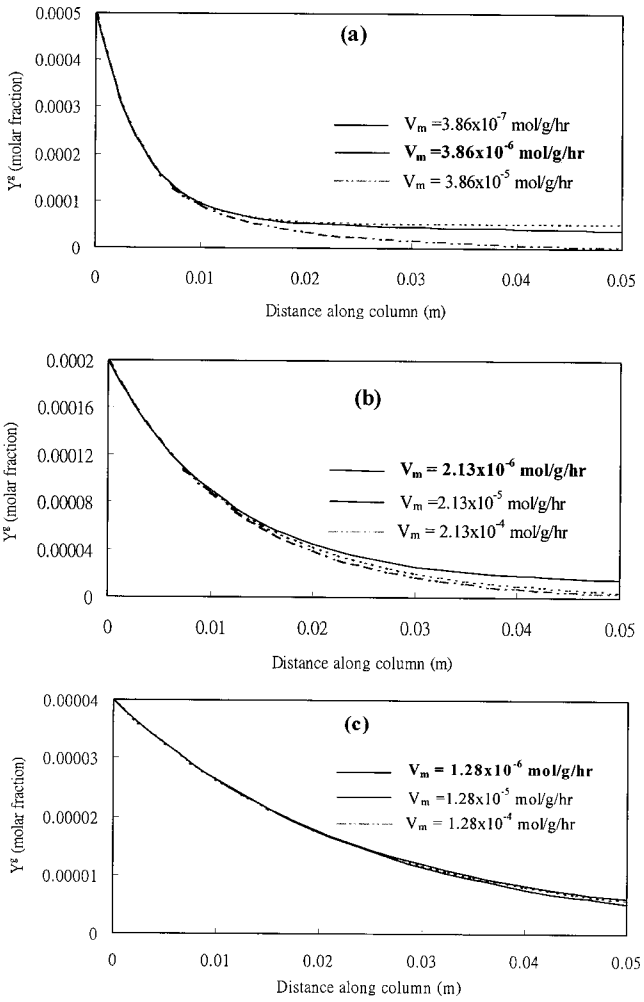

Fig. 8. Simulation of steady-state removal profiles to evaluate effects of mass-transfer resistance and biodegradation rates for (a) acetone, (b) toluene, and (c) trichloroethylene. Profiles were based on three different values of V_m, with experimental values in bold.

model simulations were performed to evaluate the limiting factors in the removal of the VOCs. The results demonstrated that removal of acetone was primarily reaction limited, whereas the removals of toluene and TCE were at least partially mass-transfer limited, particularly for TCE.

Acknowledgment

This study was partially funded by the National Nano Device Laboratories (NDL), Taiwan, Republic of China.

Notation

The following symbols are used in this paper:

a = specific area of medium (m^{-1});
C_e = effluent VOC cocentration (ppmv);
C_g = gas phase VOC concentration (ppmv);
C_L = liquid phase VOC concentration (ppmv);
C_0 = inlet VOC concentration (ppmv);
G = volumetric air flow rate (m^3/h);
H_c = Henry's law constant (atm·m^3/mol);
$K_l a$ = liquid mass-transfer coefficient (h^{-1});
K_s = saturation constant (ppmv);
L = volumetric liquid flow rate (m^3/h);
R = universal gas constant (atm·m^3/mol·K);
R_r = VOC removal rate (g VOC/h/kg medium);
R_{VOC} = VOC biodegradability (ppmv/h/10^8 cell);
S = column cross-sectional area (m^2);
SV = space velocity (h^{-1});
T = operating temperature (K);
V_f = total volume of flask (m^3);
V_L = volume of liquid in flask (m^3);
V_m = maximum VOC removal rate (g VOC/h/kg medium);
X = biofilm mass per medium surface area (g/m^2);
Y^g = gas-phase VOC concentration in mole fraction;
Y^l = liquid-phase VOC concentration in mole fraction;
Z = column packing depth (m); and
α = conversion coefficient (kg medium/g VOC).

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