TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **55**:200–209

# Evaluation of Trickle-Bed Air Biofilter Performance under Periodic Stressed Operating Conditions as a Function of Styrene Loading

**Daekeun Kim, Zhangli Cai, and George A. Sorial**
*Department of Civil and Environmental Engineering at the University of Cincinnati, Cincinnati, OH*

## ABSTRACT

Trickle-bed air biofilters (TBABs) are suitable for treating volatile organic compounds (VOCs) at a significantly high practical loading because of their controlled environmental conditions. The application of TBAB for treating styrene-contaminated air under periodic backwashing and cyclical nonuse periods at a styrene loading of 0.64–3.17 kg chemical oxygen demand (COD)/m$^3$·day was the main focus of this study.

Consistent long-term efficient performance of TBAB strongly depended on biomass control. A periodic in situ upflow with nutrient solution under media fluidization, that is, backwashing, was approached in this study. Two different nonuse periods were employed to simulate a shutdown for equipment repair or during weekends and holidays. The first is a starvation period without styrene loading, and the second is a stagnant period, which reflects no flow passing through the biofilter.

For styrene loadings up to 1.9 kg COD/m$^3$·day, removal efficiencies consistently above 99% were achieved by conducting a coordinated biomass control strategy, that is, backwashing for 1 hr once per week. Under cyclical nonuse periods for styrene loadings up to 1.27 kg COD/m$^3$·day, stable long-term performance of the biofilter was maintained at more than 99% removal without employing backwashing. No substantial impact of nonuse periods on the biofilter performance was revealed. However, a coordinated biomass control by backwashing subsequently was unavoidable for attaining consistently high removal efficiency at a styrene loading of 3.17 kg COD/m$^3$·day.

As styrene loading was increased, reacclimation of the biofilter to reach the 99% removal efficiency following backwashing or the nonuse periods was delayed. After the nonuse periods, the response of the biofilter was a strong function of the biomass in the bed. No significant difference between the effects of the two different nonuse periods on TBAB performance was observed during the study period.

### IMPLICATIONS

In practice, a biofilter is exposed to nonuse periods such as a shutdown for retooling or repair, or during weekends and holidays. Also, most off-gas streams contaminated with VOCs have variable flow rates and unsteady loadings, which limit the application of air biofiltration systems. This paper evaluated the impact of nonuse periods on biofilter performance as a function of styrene loading. The obtained results were compared against the consistently high efficient performance of the biofilter by employing backwashing as biomass control. The study results can be taken into consideration in the design and operation of the TBAB for full-scale application.

## INTRODUCTION

Many air pollutants of concern are volatile organic compounds (VOCs) that are of environmental concern because of their toxicity. In particular, styrene is primarily a synthetic chemical that is used extensively as a starting material for the production of synthetic polymers, such as polystyrene, and as a solvent in the polymer processing industry.[1] The release of styrene into the environment can occur by a variety of routes, including wastewater discharges from factories and evaporation, pyrolysis of polystyrene, and paints.[2] Styrene also is known as vinylbenzene, ethenylbenzene, cinnamene, or phenylethylene. It is a colorless, volatile, strongly smelling liquid. Chronic exposure to styrene has been considered to be responsible for mutagenic, genotoxic, and carcinogenic effects.[3] It is therefore classified as a possible human carcinogen by the U.S. Environmental Protection Agency (EPA) and by the International Agency for Research on Cancer. Furthermore, styrene is one of the 188 hazardous air pollutants listed in the Clean Air Act Amendment. Because styrene concentration in industrial waste gas is at a low level in most cases, biological technologies are recognized to be attractive as compared with other controls, such as thermal incineration, carbon adsorption, liquid scrubbing, condensation, and catalytic incineration.[4] Biological air pollution technologies convert the pollutants to nonhazardous materials within the treated stream before their release to the environment. In recent years, biofiltration has been recognized as a cost-effective technology for the purification of air contaminated with low concentrations of biologically degradable organic compounds.[5,6] Biofilters have been designed primarily for odor control at wastewater treatment plants, composting plants, and industrial processes. This is rapidly becoming a promising air pollution control technology for removing VOCs present in waste airstreams. Conventional biofilters use a natural organic medium such as peat, compost, leaves, wood bark, or soil. The natural organic medium is impregnated with solid nutrients and buffers, and the bed moisture is maintained at a constant level by humidifying air.

TBAB is conceptually an identical process to the biofilter. TBABs employ synthetic inorganic or polymeric media as microbial attachments and allow intermittent delivery of nutrient and buffer to the media bed. The concept of the TBAB allows consistent nutrient and pH control for optimizing the waste-utilizing kinetics for microorganisms. TBABs employing synthetic, inorganic media as microbial attachments are especially applicable for treating VOCs at high loading.[7,8] TBABs achieved consistent VOC removal efficiencies exceeding 99% at high VOC loadings.[2,5] However, the biofilter performance decreased substantially, coincident with the buildup of back pressure caused by the accumulation of excess biomass within the medium bed.[8–11] The control of biomass was necessary for attaining stable, long-term high removal efficiencies for the biofilter. For this reason, some reports have focused on biomass control for long-term operation of biofiltration. Reported biomass control strategies include bed irrigation,[11] stimulation of protozoan predation,[12] mechanical methods employing bed stirring and bed washing[9] and sodium hydroxide washing,[10] and periodic backwashing with full-medium fluidization.[2,5,7,8] Most of these methods have major drawbacks, such as the subsequent reduction in biofilter performance because of the loss of active biomass.[9] The reported studies employing the periodic backwashing strategy demonstrated that the long-term performance of biofilters could be maintained at high removal efficiencies in the 99% level for a toluene loading of 4.1 kg chemical oxygen demand (COD)/$m^3$·day[5] and for a styrene loading of 4.26 kg COD/$m^3$·day.[2] However, because biomass buildup is related mainly to contaminant loading in the biofilter,[7] fluctuations in performance will occur when there are sudden changes in contaminant loading and insufficient time for microbial reacclimation after conducting the biomass control strategy.

In practice, most off-gas contaminated with VOCs has variable flow rates, unsteady loading, and various contaminant compositions, which limit the handling efficiency of the biofiltration.[13] During unsteady loading, biofilter acclimation needs to be known to determine the optimum conditions that will provide a constant outlet contaminant concentration. The biofilter also is exposed to the chemical starvation conditions because of the shutdown for equipment repair or during weekends and holidays. Generally, the original removal efficiencies after starvation periods can be recovered more quickly than those seen in the original acclimation at the startup. The study of microbial activity in a biomass recycle reactor revealed that starvation resulted in a variation in bacterial numbers and microbial community as well as their physiological state.[14] Some studies reported biofilter performance under chemical starvation conditions.[11,13,15,16] Fitch et al. studied biofiltration for 1-butanol removal under continuous and diurnal loading conditions and reported that diurnal operation did not contribute to a decrease in biofilter efficiency as compared with continuous operation.[13] Most of these studies were concerned mainly with the reacclimation periods and the duration and mode of starvation. However, few studies discussed the effect of the starvation condition on the biofilter performance as a function of contaminant loading.

The objectives of this research were, therefore, to investigate the performance of a TBAB under periodic stressed operating conditions as a function of styrene loading. The goal was to evaluate the effect of backwashing and nonuse periods on the performance of a TBAB for long-term operation. The evaluations are focused on the following operational parameters: (1) styrene loading and styrene removal rate, (2) the response of biofilter performance after backwashing and nonuse periods, (3) development of preliminary kinetic data based on removal with biofilter depth, (4) nitrogen utilization and styrene removal, and (5) carbon dioxide ($CO_2$) production and carbon balance.

## MATERIALS AND METHODS

### Experimental Biofilter System

The experimental system for the laboratory-scale TBAB is presented in Figure 1. The biofilter was constructed of seven cylindrical glass sections (Ace Glass, Inc.) with an internal diameter of 76 mm and a total length of 130 cm. The sections were connected with high-pressure clamps (75 psi). Each section was equipped with a sampling port that extends to the center of the column. A headspace section in the top section was designed for a VOC-containing air inlet and for housing the nutrient spray nozzle, while a bottom space at the bottom section was designed for the outlet of treated air and leachate. Each space had sampling ports to allow sampling of stream entering and leaving the biofilter, as well as axially along the medium bed four gas-sampling ports, which were located at 7.6, 23, 38, and 53 cm from the bottom of bed of the reactor. The reactor was packed with pelletized diatomaceous earth biological support media (Celite 6 mm R-635 Bio-Catalyst Carrier; Celite Corp.) to a depth of ~60 cm. The pelletized medium was demonstrated to be

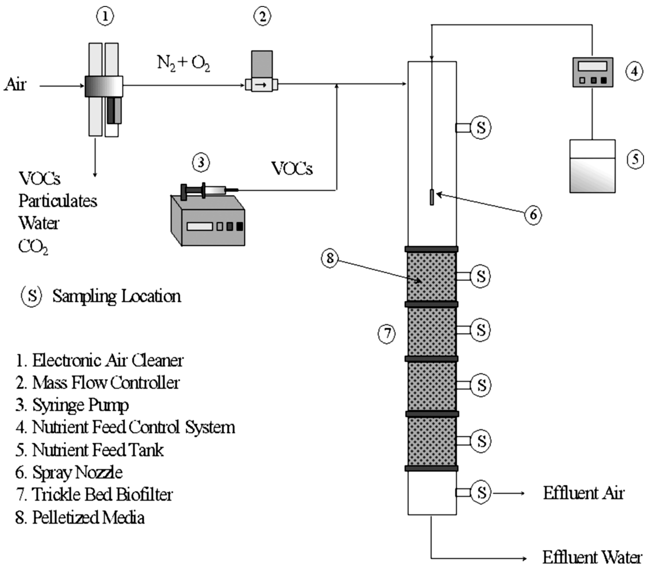

**Figure 1.** The experimental setup.

significantly superior to the other media, such as a compost mixture and a synthetic, monolithic media.[17] The pellets of R-635 were made from sintered diatomaceous earth and are, therefore, principally silica. Their physical properties were measured in a previous study[8] performed at the University of Cincinnati. They had a circular cross section with a nominal diameter of 0.635 cm, a length of 0.64 cm (mean), a sphericity of 0.84, and a specific surface of 11.9 $cm^2/cm^3$. The measured pellet internal and external void fractions were ~0.65 and 0.34, respectively, and the bulk density was ~0.62 $g/cm^3$. The biofilter was maintained at a constant operating temperature of 20 °C in a constant temperature chamber. The biofilter was operated in a cocurrent gas and liquid downward flow mode.

The air supplied to the biofilter was purified with complete removal of water, oil, $CO_2$, VOCs, and particles by Balston FTIR purge gas generator (Paker Hannifin Corp.). The air pressure was reduced to 20 psi (140 kPa) by a pressure control valve, both for safety and for isolating the biofilter from any pressure fluctuations in the upstream air supply. The airflow to the biofilter was set up at a rate of 3.6 L/min (initial setup value), regulated by a mass flow controller (MKS Model 247C four-channel read-out mass flow controller). Liquid VOC was injected via a syringe pump (Harvard Apparatus, model NP 70–2208) into the airstream where it vaporized and entered the biofilter through the topmost side port of the column.

The biofilter was equipped with an independent system for feeding 1.5 L/day (initial setup value) of a buffered nutrient solution. This solution was made from deionized and activated carbon filtered water, according to a formulation that contains all necessary macronutrients, micronutrients, and buffers, as described in a previous study.[2] The nutrient formulation for the biofilter was adjusted to contain the same amount (wt/wt) of nutrient nitrogen (N) and phosphorus (P) for a given VOC loading (COD/N = 50 and N/P = 4). As the sole source of nutrient N, nitrate ($NO_3$-N) was used because the use of $NO_3$-N instead of ammonia ($NH_3$-N) can be effective in reducing the observed biomass yield and provided better performance of biofilter.[8] One molar sodium bicarbonate was used as a pH buffer. The solution was circulated by a stainless-steel gear pump from a 20-L feed tank through a solenoid-operated three-way valve and back to the feed tank. A programmable controller (Danaher Controls, Eagle Signal Model MX 190) activated the solenoid once per minute to divert the feed to the biofilter so that a set feeding rate was provided per day. The feed was sprayed as a fine mist onto the top of the medium bed through a spray nozzle (Corrigan Corp.).

### Materials

Reagent-grade styrene (99%, Fisher Scientific Co., Inc.) was used as the sole VOC contaminant in this study. All chemicals used in preparation of the nutrient feed solutions were of reagent or equivalent high-purity grade. The microbial seed for the biofilter was obtained from the secondary clarifier of the activated sludge system at a municipal wastewater treatment plant (Millcreek Wastewater Treatment Plant).

### Analytical Methods

Gas-phase samples for styrene analysis were taken with gas-tight syringes through low-bleed and high-puncture-tolerance silicone gas chromatograph (GC) septa installed in the sampling ports. The concentration of styrene as gas phase was determined by using a GC (HP 5890, Series II, Hewlett Packard) with a flame-ionization detector (FID) and a 30-m narrow bore column (DB 624, J&W Scientific). The GC oven temperature was programmed from 40 to 120 °C at rate of 20 °C/min with a 2-min hold at 40 °C and a 2-min hold at 120 °C. The carrier gas (nitrogen; $N_2$) flow rate was set at 2.3 mL/min. The FID detector was used with $N_2$ makeup gas at a flow rate of 20 mL/min, a fuel gas flow (hydrogen) of 30 mL/min, and an oxidizing gas flow (air) of 300 mL/min. The detector temperature was 250 °C. The retention time of styrene was 4.9 min under the conditions used.

Effluent gas-phase samples for $CO_2$ analysis also were taken by using gas-tight syringes through the sampling port in the biofilter. A GC equipped with a thermal conductivity detector (TCD) was used for determining the $CO_2$ concentrations. The GC oven temperature was programmed from 50 to 80 °C at 10 °C/min with a 3.2 min hold at 50 °C and a 1.5 min hold at 80 °C. The carrier gas (helium; He) flow rate was set at 30 mL/min, and the TCD detector was used with He makeup gas at flow rate of 35 $\mu$L/min.

Liquid-phase sample were analyzed for $NO_3^-$, total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. $NO_3^-$ was determined by using a Shimadzu UVmini 1240 UV-VIS spectrophotometer (Shimadzu Corp.). TC and IC were determined by using a Shimadzu TOC 5000 analyzer (Shimadzu Corp.). Samples were filtered through 0.45-μm nylon filters (Micron Separation) before analysis. The VSS concentration in the effluent and backwashing water were determined according to Standard Methods 2540 G.[18] The pH was determined using a Fisher Accumet pH meter, Model 50 (Fisher Scientific Co., Inc.). The pH meter was calibrated by using buffers (pH 4, 7, and 10) supplied by the manufacturer. Pressure drop along the biofilter was monitored by a digital manometer (Modus Instruments, Inc.).

### Experimental Plan

The biofilter was operated with six experimental stages according to styrene inlet concentrations and loading, which are summarized in Table 1. Each experimental strategy is divided into three parts. The first involves the study of the performance of a biofilter under backwashing as the biomass control. The remaining two focused on two different types of nonuse periods (namely, the starvation period and the stagnant period).

*Backwashing.* Backwashing was conducted while the biofilter was offline by first using 18 L of the buffered nutrient solution to induce full medium fluidization at ~50% bed expansion for a defined time period. Finally, the recycle was shut off and 18 L of the buffered nutrient solution was passed through the column as a rinse. The backwashing duration and frequency initially were set at 1 hr once per week for each styrene loading. Compressed air at a rate of ~20 L/min was introduced at the bottom of the biofilter when necessary for shearing off excess biomass.

**Table 1.** Experimental plan and operating conditions.

| | Stage I | Stage II | Stage III | Stage IV | Stage V | Stage VI |
|---|---|---|---|---|---|---|
| Operating Condition | | | | | | |
| Inlet concentration (ppmv styrene) | 50 | 50 | 100 | 250 | 330 | 200 |
| EBRT (min) | 0.76 | 1.51 | 1.51 | 1.51 | 2.02 | 2.02 |
| Styrene loading (kg COD/m$^3$·day) | 1.27 | 0.64 | 1.27 | 3.17 | 3.17 | 1.9 |
| Experimental Strategy | Operational Periods in Days | | | | | |
| Backwashing | 1–43 | 44–50 | 92–113 | 155–194 | 195–210 | 258–272 |
| Starvation | | 51–70 | 114–134 | | 211–231 | |
| Stagnant | | 71–91 | 135–154 | | 232–257 | |

*Starvation Period.* This experimental strategy involves the period without styrene loading, which means pure air with nutrient flow through the biofilter. The duration and frequency for this strategy were two days per week for a period of 3 weeks at styrene loadings of 0.64, 1.27, and 3.17 kg COD/m$^3$·day.

*Stagnant Period.* This experimental strategy reflects no flow (styrene, nutrient, and air) passing through the biofilter. The duration and frequency for this strategy were two days per week for a period of 3 weeks at styrene loadings of 0.64, 1.27, and 3.17 kg COD/m$^3$·day.

## RESULTS AND DISCUSSIONS

The biofilter was filled with virgin Celite pellets. The pellets initially were seeded with an aerobic microbial culture. Before seeding, 100 g/L of a glucose solution as the primary substrate was introduced over the bed and allowed within the bed for a period of 30 min. The bed then was flooded with the decanted water of the collected activated sludge for a period of 30 min. The biofilter system was then started by introducing the buffered nutrient solution and the contaminated air.

### Performance of the Biofilter

The biofilter was started up using an influent styrene concentration of 50 ppmv, 0.76 min EBRT (1.27 kg COD/m$^3$·day), and 2.25 mmol $NO_3$-N per day as the sole N source (stage I). By day 19, the overall removal efficiency was unstable even though it had risen to 97% on day 13. At this point, it was discovered that an error had been made in the preparation of the buffered nutrient solutions for the biofilter, which had a high pH (over pH 8.7). The buffered nutrient solutions then were adjusted to approximately pH 8 on day 20. After that, the effluent pH was stable at pH 8–8.5. The styrene removal efficiency then had reached to more than 95% and remained at this level for 5 days. On day 28, the biofilter was backwashed for the first time. After backwashing, the overall removal efficiency increased to 99%. But, it dropped to as low as 80% by the day before the following backwashing. On day 47, when backwashing was conducted, the EBRT was increased to 1.51 min and the inlet styrene concentration still was maintained at 50 ppmv, corresponding to a loading of 0.64 kg COD/m$^3$·day (Stage II). The removal efficiency increased to the 99% level and remained stable at this level. During this experimental period, four cycles of backwashing were conducted. After each backwash, the biofilter regained a removal efficiency of more than 99% on the following day. The biofilter performance with respect to styrene removal is shown in Figure 2.

On days 52 and 53, the styrene loading to the biofilter was stopped to start the first cycle of the starvation period

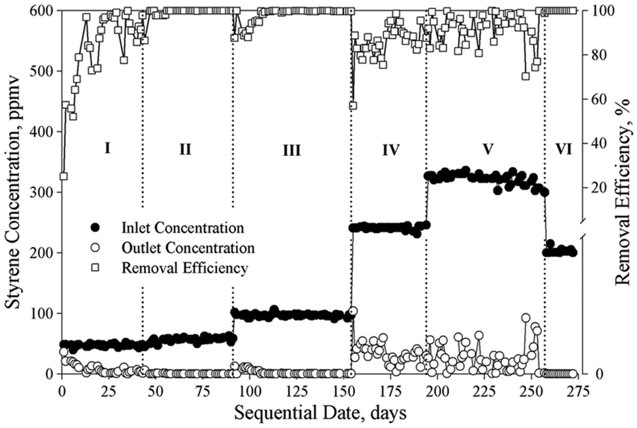

**Figure 2.** Biofilter performance with respect to styrene removal.

strategy. After re-startup on day 54, the removal efficiency recovered to 99% within 300 min and remained above 99% without the backwashing strategy during the three cycles. On days 73 and 74, styrene, nutrients, and air were stopped to conduct the first cycle of the stagnant period strategy. After re-startup following two days of the shutdown, the removal efficiency recovered to 99% within 300 min and remained above 99% without the backwashing strategy during the three cycles. During the nonuse period strategies, pressure drop stabilized at ~1 cm of water, indicating that biomass had been kept consistently in the system during the operation of these strategies.

On day 92, when backwashing was conducted, the inlet concentration was increased to 100 ppmv corresponding to a loading of 1.27 kg COD/m$^3$·day (Stage III). The $NO_3$-N feed rate was increased accordingly to ~4.5 mmol/day. The removal efficiency dropped to below 90%, and the biofilter did not reach the 99% performance level for 12 days. To recover the desired high removal efficiency, on day 104, the feed rate of the buffered nutrient solution was increased from 1.5 to 2.4 L/day, corresponding to a 7.2 mmol/day $NO_3$-N feed rate. On the third day, the overall removal efficiency was more than 99% and remained at this level. A similar behavior was observed by Zhu et al.[19] in their biofiltration study of diethyl ether. They indicated that a higher flow rate of nutrient liquid might result in better biofilter performance because of the increase in the nutrient diffusion driving force.

On days 115 and 116, the styrene loading to the biofilter was stopped as the first cycle of the starvation period at the styrene loading of 1.27 kg COD/m$^3$·day. After re-startup on day 117, the removal efficiency recovered to 99% within 10 hr and remained at the 99% removal efficiency without the backwashing strategy during the three cycles. On days 136 and 137, the first cycle of the stagnant period strategy at a styrene loading of 1.27 kg COD/m$^3$·day was conducted. After re-startup on day 138, the biofilter still was maintained at 99% performance level without the backwashing strategy. Furthermore, it was noticed that, during the nonuse period strategy for 1.27 kg COD/m$^3$·day, the appearance of the pellets was similar to those seen during operation of the biofilter with the nonuse period for 0.64 kg COD/m$^3$·day, that is, grayish to medium brown.

On day 155, when backwashing was conducted, the inlet concentration was increased to 250 ppmv with a corresponding loading of 3.17 kg COD/m$^3$·day (Stage IV). The $NO_3$-N feed rate was increased accordingly to ~18 mmol/day. After an increase in inlet concentration, the removal efficiency dropped below 57% and then increased to 89% by the following day. But, by day 194, the overall removal efficiency had not reached the 99% level even though it had risen to 99% just after the backwashing on day 178. On day 195, the EBRT was increased to 2.02 min and the styrene loading still was maintained at 3.17 kg COD/m$^3$·day, corresponding to an inlet styrene concentration of 330 ppmv (Stage V). Subsequently, styrene removal efficiency increased to 99% one day after backwashing, but it dropped to as low as 80% by the day before the following backwashing.

On days 209 and 210, the first cycle of the starvation period at a styrene loading of 3.17 kg COD/m$^3$·day was conducted. After restart-up, the overall removal efficiency had risen to 96% by the next day, and then it decreased to 85%. A similar performance of the biofilter was observed after the second cycle of the starvation period. This poor performance might be caused by the excess biomass that had accumulated within the biofilter. Therefore, on day 223, backwashing was conducted as a means for biomass control. The removal efficiency then increased to 98% by the next day. After the third cycle of the starvation period, the overall removal efficiency had risen to 99%, but it did not remain at this level. At this point, the first cycle of the stagnant period was conducted together with the backwashing. The removal efficiency increased to 99% by the next day after re-startup and remained at the 95% level. The second cycle of the stagnant period was conducted without backwashing, and the overall removal efficiency decreased to 70%. After the third cycle of the stagnant period (without backwashing), the overall removal efficiency was 90% at re-startup and then dropped to 75%. However, one day after the backwashing on day 253, the biofilter regained removal efficiency of more than 99%. When the stagnant period strategy was conducted once more with backwashing, the overall removal efficiency remained at the 99% level. It is interesting to note that the behavior of the biofilter depended on biomass control because the biofilter performance decreased substantially with buildup of back pressure because of accumulation of excess biomass.[7–9,11]

On day 259, when backwashing was conducted, the inlet concentration was decreased to 200 ppmv with a corresponding loading of 2.53 kg COD/m$^3$·day (Stage VI). The removal efficiency generally remained at 99% with backwashing at a rate of 1 hr/week. In a previous study of styrene biofiltration[2] using backwashing with a duration of 2 hr every other day, the maximum styrene removal rate was 4.26 kg COD/m$^3$·day (57.8 g/m$^3$·hr) with removal efficiencies in the 97–99% level. Thus, a more frequent and longer duration of backwashing was perceived as contributing to the consistently high removal efficiencies at high styrene loadings.

Table 2 presents reported biofilter performances for styrene removal. In this table, high elimination capacities are noted for the biofilters seeded by specific or adapted microorganisms. In general, the biofilters with natural media or activated sludge inoculum generally need long acclimation periods to achieve high elimination capacities, while the biofilters with specific or adapted microorganisms decrease the acclimation periods and obtain high elimination capacities.[20] On the other hand, higher removal efficiencies are revealed for the trickle biofilter with backwashing as biomass control. Specifically, the biofilter employed in this study had a consistently high removal efficiency (>99%) even at high inlet concentration (0.87 g/m$^3$).

An excess of oxygen ($O_2$) as an electron acceptor has to exist throughout the entire biofilm to avoid biofilter failure.[21] Based on the maximum equilibrium concentration of $O_2$ in the biofilm at the air-biofilm interface, the maximum practical concentration for styrene in the biofilm at the interface was deduced to be 257 ppmv at 32.2 °C.[2] It is shown in Figure 3 that styrene loadings above 1.9 kg COD/m$^3$·day lead to a decrease in biofilter efficiency. This value corresponds to an inlet styrene concentration

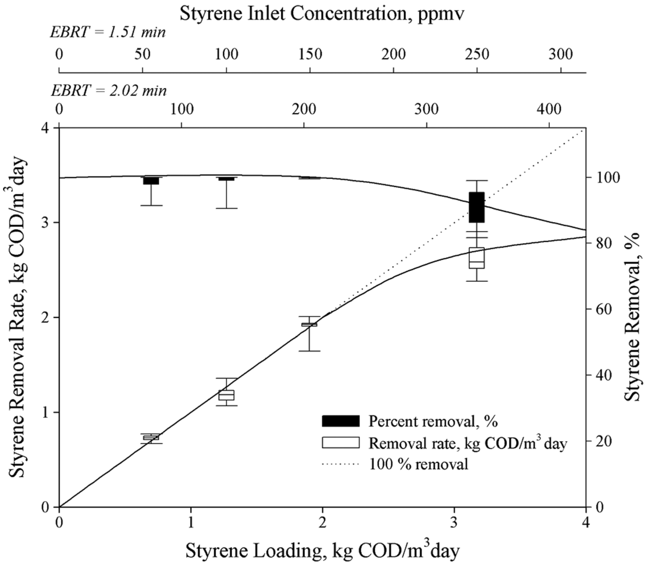

**Figure 3.** Styrene removal vs. styrene loading rate and the corresponding inlet concentration.

**Table 2.** Comparison of biofilter performance for styrene removal.

| Type | Medium | Loading (g/m$^3$·hr) | Inlet Conc. (g/m$^3$) | Elimination Capacity (g/m$^3$·hr) | Removal (%) | Bed Seeded by | Biomass Control | Reference |
|---|---|---|---|---|---|---|---|---|
| Trickle biofilter | Pellet | <25.8 | <0.87 | <25.8 | >99 | Activated sludge | Backwashing[a] | This study |
| Trickle biofilter | Pellet | <57.8 | <0.69 | <57.8 | 97–99 | The decanted pellet wash water from toluene biofilter | Backwashing[b] | 2 |
| Trickle biofilter | Plastic spheres | -[c] | <0.8 | 23–35 | 70–80 | - | - | 23 |
| Trickle biofilter | Peat and glass beads | 6.14–588 | 0.05–1.2 | <63 | - | *Rhodococcus rhodochrous AL* NCIMB 13259 | - | 24 |
| Trickle biofilter | Coal particles | 6–96 | - | <70 | >75 | Activated sludge | - | 25 |
| Trickle biofilter | Pellet | <164.4 | 1.01 | <141 | 86 ± 7 | Microbial consortium | Bed irrigation | 11 |
| Trickle biofilter | Slag | <51 | <2.74 | <45.2 | >90 | Activated sludge | No | 4 |
| Biofilter | Mixture of Perlite, mineral medium, and fungi | <75 | 0.022–0.11 | <62[d] | - | *Exophiala jeanselmei* | - | 26 |
| Biofilter | Composted wood bark and yard waste | <350 | - | 69–118 | 65–75 | Styrene—utilizing mixed microbial culture | - | 20 |
| Biofilter | Perlite | - | 0.2–1 | <140 | >90 | Media from 16 months—operated, styrene degrading biofilter | - | 27 |
| Biofilter | Peat | - | 0.05–1.2 | <30 | 70 | Activated sludge | - | 28 |

[a]The backwashing frequency and duration were set at 1 hr once per week; [b]The backwashing frequency and duration were set at 2 hr every other day; [c]Not available; [d]The maximal styrene elimination capacity increased to 91 g/m$^3$·hr by increasing the $O_2$ concentration in the gas from 20 to 40%.

of 210 ppmv for 2.02 min EBRT or 160 ppmv for 1.51 min EBRT. It is, therefore, speculated that, at inlet styrene concentrations of more than 210 ppmv for 2.02 min EBRT (or 160 ppmv for 1.51 EBRT), an unfavorable performance of biofilter is manifested.

### Biofilter Response after Backwashing and Nonuse Periods

Effluent samples were collected at prescheduled time intervals to evaluate the biofilter response subsequent to the backwashing and the nonuse periods. Figure 4 shows the effluent response corresponding to backwashing and nonuse periods for each inlet styrene loading of 0.64, 1.27, and 3.17 kg COD/m$^3$·day studied. The reacclimation period was considered to have been achieved when 99% of the original biofilter performance was attained. The following observations can be deduced from Figure 4:

(1) Reacclimation of overall biofilter performance was delayed primarily as styrene loading was increased.

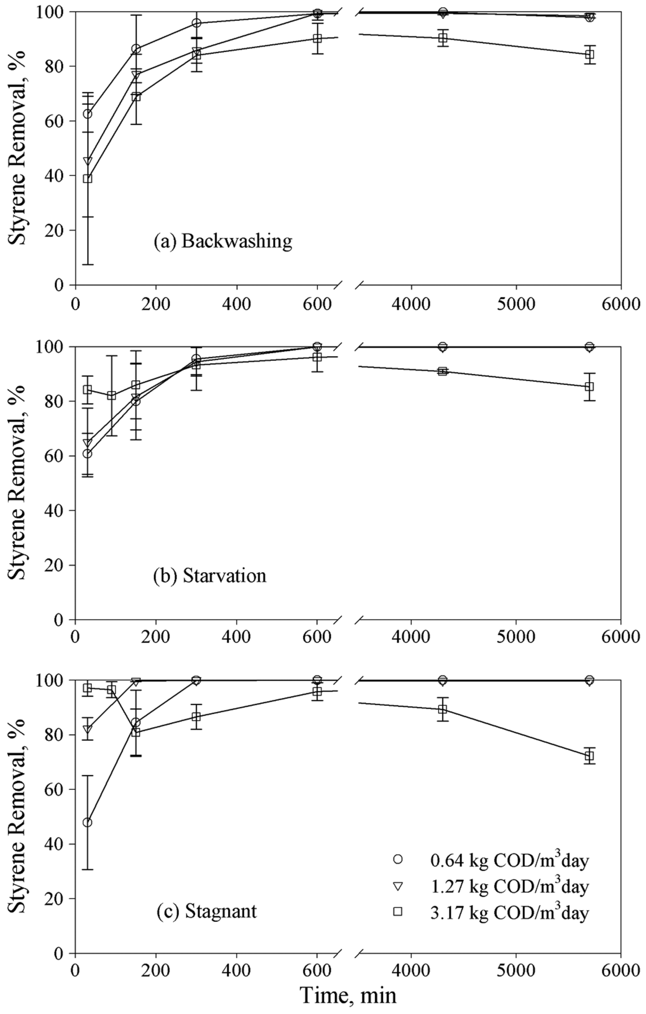

**Figure 4.** Effluent response corresponding to the backwashing and nonuse periods for different styrene loadings.

(2) For styrene loadings of 0.64 and 1.27 kg COD/m$^3$·day, the sequence of reacclimation period was in the same sequence of the experimental strategies with backwashing > starvation period > stagnant period.

(3) For styrene loadings of 3.17 kg COD/m$^3$·day, higher removal efficiency was observed in the initial time after the re-startup following nonuse periods (starvation period and stagnant period). It is speculated that, initially, adsorption of styrene on the biomass might have occurred because more biomass was available on the media of the biofilter. After a certain period, likely after breakthrough, the biofilter performance was similar to that after backwashing.

### Kinetic Analysis of Biofilter Performance

The removal performances as a function of depth in the biofilter were studied one day following the backwashing and the nonuse periods. The obtained data were used to develop the first-order removal rate as a function of depth in the biofilter for each experimental strategy. To avoid misinterpretation of the data because of the possibility of biodegradation occurring above the media bed along the reactor freeboard walls at the top of the biofilter and in the bottom disengagement chamber used for separation between water and air, the kinetic analyses were conducted by using the data from sampling ports within the media. Linear regression analysis was used for obtaining the first-order removal rate constants. The obtained results are shown in Figure 5. It can be seen clearly that the styrene reaction rate decreased as styrene loadings increased, indicating that high styrene loading can cause poor performance of the biofilter because of accumulation of excess biomass. It was especially noticed that the pellet mass seemed to be stickier or more gelatinous at high styrene loadings. For styrene loadings of 0.64 and 1.27 kg COD/m$^3$·day, the stagnant strategy showed the

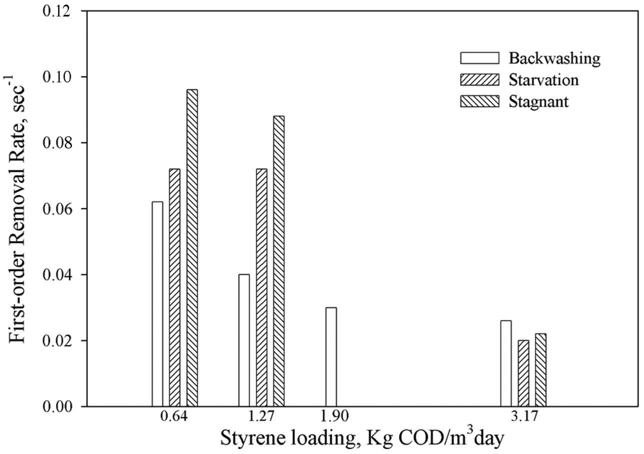

**Figure 5.** Reaction rates as a function of styrene loading.

highest reaction rate. However, this might not indicate that the biofilter had the best performance under the stagnant strategy. It is more likely because the biofilter had acclimated to the stressed operating conditions. On the other hand, it is valuable to note that the nonuse periods had little significant impact on the performance of biofilter at styrene loadings of 0.64 and 1.27 kg COD/$m^3$·day as compared with the biofilter performance under the backwashing strategy (see Figure 5).

### Nitrogen Utilization and VOC Removal

Analyses for influent and effluent concentration of $NO_3^-$ were conducted. The net N utilization was calculated by subtracting the molar amounts for the N species in the effluent from the N species present in the nutrient feed. COD removal was calculated as the difference between the COD of the feed and the COD of the effluent gas and liquid stream. The influent COD was calculated as the sum of the COD equivalent of styrene present in the inlet gas stream and the COD measured in the nutrient feed. Similarly, the effluent COD was calculated as the sum of COD-equivalent styrene present in the outlet gas and the COD measured in the effluent water.

Figure 6 shows a plot of N utilization versus styrene removal for each experimental strategy. To avoid misinterpretation of the data for the nonuse periods, the data for styrene loading of 3.17 kg COD/$m^3$·day was excluded because backwashing was conducted together with the nonuse periods. Table 3 gives two estimates of the COD/N and yield (VSS/COD). Assuming the COD/N utilization was independent of loading and that aerobic heterotrophic organisms accounted for the net N utilization, the estimate of the COD/N was obtained from the inverse of the slope of the regression line of Figure 6. The ratio of the mass of VSS produced to the mass of COD removed was estimated by assuming VSS is 14% N. Statistical analysis also was made by calculating the ratio of COD/N for each data point and determining the average value. Also in Table 3, the corresponding values of COD/N and yield (VSS/COD) for styrene obtained in a previous study[2] are given. The results shown in Table 3 show no significant difference between the corresponding values of yield (VSS/COD) for the two different nonuse period strategies (the starvation period and the stagnant period), while the yield (VSS/chemical oxygen demand) for the two different nonuse period strategies is much lower than that for the backwashing strategy. Furthermore, it is noted that the estimates for the two nonuse period strategies are less reliable because of low $R^2$ values and high standard deviations (see Table 3).

**Table 3.** g COD/ g N and equivalent VSS yields.

| | This Study | | | Sorial et al.[2] |
|---|---|---|---|---|
| | Backwashing | Starvation | Stagnant | |
| Graphical Analysis | | | | |
| g COD/g N | 62.1 | 88.5 | 95.2 | 70.4 |
| $R^2$ | 0.837 | 0.461 | 0.447 | 0.89 |
| g VSS/g COD (yield) | 0.115 | 0.081 | 0.075 | 0.101 |
| Statistical Analysis | | | | |
| g COD/g N | 70.8 | 126 | 123 | 75.8 |
| SD | 20.2 | 99.2 | 58.7 | 23.9 |
| g VSS/g COD (yield) | 0.101 | 0.057 | 0.058 | 0.094 |

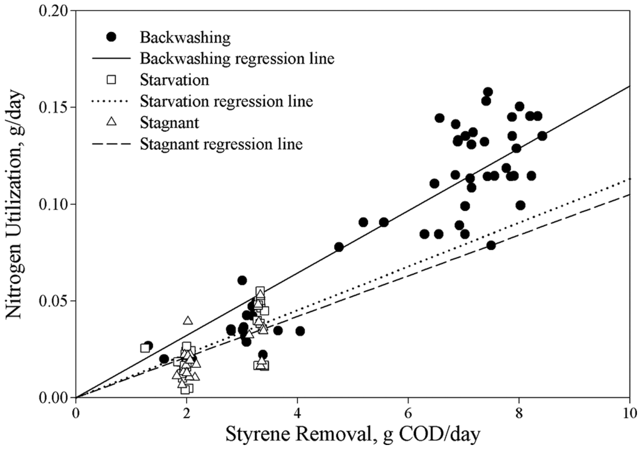

**Figure 6.** Utilization of N as a function of COD removal for the experimental strategies.

Figure 7 shows COD/N ratios plotted against the sequential date. No significant, long-term dependence of the COD/N ratio on either time or styrene loading is apparent for the backwashing strategy, while for the two nonuse period strategies, significant dependence of the COD/N ratio on time and styrene loading is manifested. First, a clear dependence on time is seen at low styrene loadings (0.64 and 1.27 kg COD/$m^3$·day—Stages I and II). High values of the COD/N ratio are noticed one day after the re-startup and then these values decrease with time approaching the values obtained for the backwashing strategy. It is speculated that aerobic chemoheterotrophs contributing to degrading styrene used the organic carbon as an energy source for the maintenance of microbial viability rather than as a carbon source for growth. In general, microorganisms grown at higher specific growth rates have higher RNA and lower protein contents than do microorganisms grown at lower specific growth rates. Moe and Irvine[22] demonstrated in their study for the periodical operation of the biofilter that the physiological state of the microbial population for the biofilter operated periodically differed from that for the biofilter operated continuously, and the periodic operation led to enhancing the contaminant removal with higher ratios of RNA to protein. Second, at a high styrene loading (3.17 kg COD/$m^3$·day), where it was noticed that backwashing was

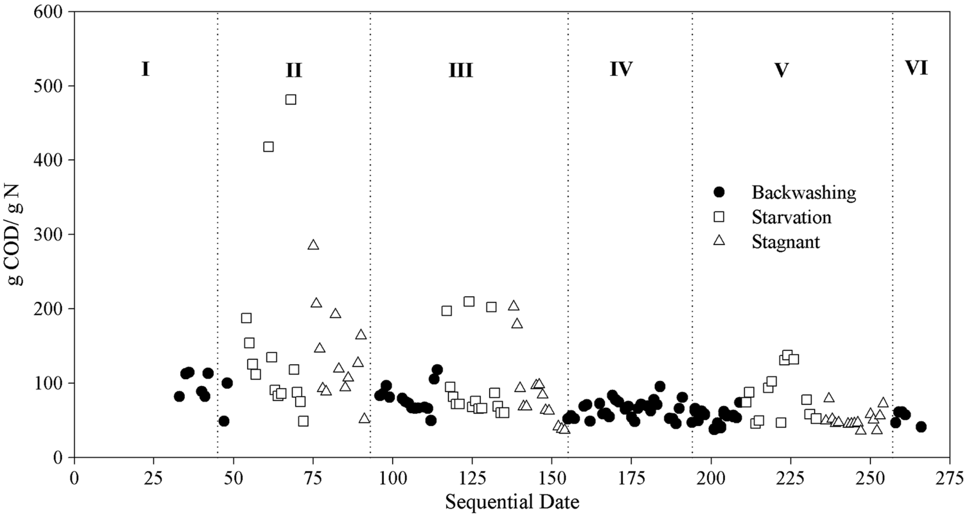

**Figure 7.** g COD/g N with respect to time.

demanded during the nonuse periods, there was little dependence of COD/N ratio on time following re-startup.

### $CO_2$ Production and Carbon Balance

Daily analyses for the influent and effluent concentrations of $CO_2$ were conducted. The net production of $CO_2$ was developed in Figure 8 as a function of the consumed styrene, indicating that the ratio of $CO_2$ production to consumed styrene is ~5.8, 6.2, and 7.5 for the backwashing, the starvation period, and the stagnant period, respectively. In the chemical oxidation of styrene to $CO_2$ and water ($C_8H_8 + 10\ O_2 \rightarrow 8\ CO_2 + 4\ H_2O$), 1 mole of styrene can produce 8 moles of $CO_2$. The difference between the experimental value and the hypothesized value may result in the production of biomass. Interestingly, the ratios of $CO_2$ to styrene consumed for the nonuse period strategies are higher than that for the backwashing strategy. This confirms that during the nonuse period strategies, most styrene consumed was utilized as the energy source for the maintenance of microbial viability, as discussed previously.

The cumulative carbon of the styrene consumed during all the experimental runs was compared with the cumulative carbon produced within the biofilter. The cumulative carbon produced was estimated as a balance of the net analysis of influent and effluent for carbon in the gas and liquid streams coupled with the VSS loss from the system. It is seen from Figure 9 that the carbon recovery was 96.9%, which is relatively good closure between the two cumulative values.

## CONCLUSIONS

This study evaluated the performance of styrene-fed TBAB operated under periodic stressed operating conditions, backwashing, and two different nonuse periods (starvation period and stagnant period), as a function of styrene loading (0.64 kg COD/$m^3$·day to 3.17 kg COD/$m^3$·day). For styrene loadings up to 1.9 kg COD/$m^3$·day, removal efficiencies consistently above 99% were achieved by conducting backwashing at a rate of 1 hr once per week. Under the nonuse periods, the biofilter performance still maintained the 99% removal efficiency without backwashing. The nonuse periods have little significant impact on the performance of biofilter for styrene loadings up to 1.27 kg COD/$m^3$·day, indicating that nonuse periods can be considered as another means of biomass control. Thus, biotrickling filters that are periodically loaded (e.g., because of weekend shutdowns) may not need backwashing to maintain bioreactor performance and optimal biofilm thickness. The maximum allowable styrene inlet concentration that will provide the 99% removal

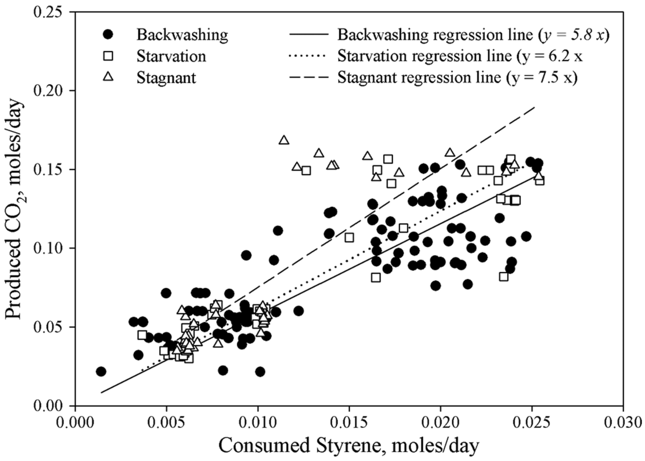

**Figure 8.** $CO_2$ production as a function of consumed styrene.

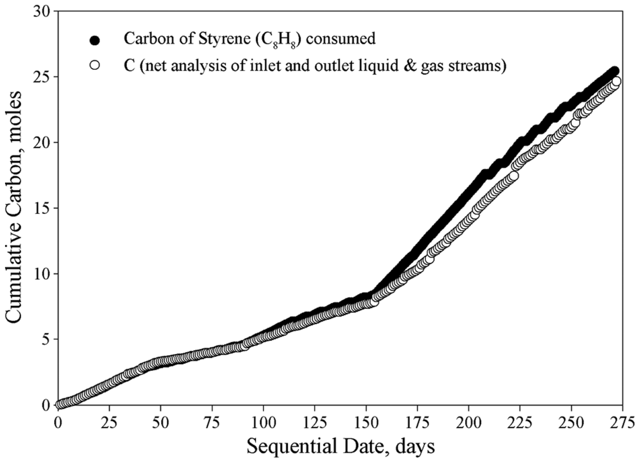

**Figure 9.** Development of carbon balance for the biofilter with time.

efficiency was demonstrated to be 210 ppmv for 2.02 min EBRT or 160 ppmv for 1.51 min EBRT with a corresponding loading of 1.9 kg COD/$m^3$·day.

The biofilter performance was evaluated further for styrene loading up to 3.17 kg COD/$m^3$·day. Styrene removal efficiency increased to 99% one day after the backwashing but dropped to as low as 80% by the day before the next backwashing. For the nonuse periods, a coordinated biomass control of backwashing was unavoidable for reaching the 99% removal efficiency because excess biomass can be accumulated within the media of the biofilter.

Following backwashing and nonuse periods, reacclimation of the biofilter to reach the 99% removal efficiency was delayed as the styrene loading increased. Reacclimation performance after the nonuse periods apparently was different to that after backwashing. The biofilter response after re-startup following the nonuse periods is a strong function of the active biomass in the system. No significant difference between the effects of two different nonuse periods on biofilter performance was observed during the period of this research.

## ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Award #BES 0229135. The finding and conclusions expressed in this publication are solely those of the authors and do not necessary reflect the views of the Foundation. The authors thank Steven Mallin and Rachel Rhodes, undergraduate students from the University of Cincinnati, for their dependable and skilled technical assistance. Sincere gratitude is also extended to Dr. Makram T. Suidan and his research assistants at the University of Cincinnati for their consistent assistance during this phase of the research.

## REFERENCES

1. O'Leary, N.D.; O'Connor, K.E.; Dobson, A.D.W. Biochemistry, Genetics and Physiology of Microbial Styrene Degradation; *Fems. Microbiol. Rev.* **2002**, *26* (4), 403-417.
2. Sorial, G.A.; Smith, F.L.; Suidan, M.T.; Pandit, A.; Biswas, P.; Brenner, R.C. Evaluation of Trickle-Bed Air Biofilter Performance for Styrene Removal; *Water Res.* **1998**, *32* (5), 1593-1603.
3. Linhart, I. Stereochemistry of Styrene Biotransformation; *Drug Metab. Rev.* **2001**, *33* (3–4), 353-367.
4. Chou, M.S.; Hsiao, C.C. Treatment of Styrene-Contaminated Airstream in Biotrickling Filter Packed with Slags; *J. Environ. Eng.-ASCE* **1998**, *124* (9), 844-850.
5. Smith, F.L.; Sorial, G.A.; Suidan, M.T.; Pandit, A.; Biswas, P.; Brenner, R.C. Evaluation of Trickle Bed Air Biofilter Performance as a Function of Inlet VOC Concentration and Loading, and Biomass Control; *J. Air & Waste Manage. Assoc.* **1998**, *48* (7), 627-636.
6. Deshusses, M.A. Biological Waste Air Treatment in Biofilters; *Curr. Opin. Biotechnol.* **1997**, *8* (3), 335-339.
7. Sorial, G.A.; Smith, F.L.; Suidan, M.T.; Biswas, P.; Brenner, R.C. Evaluation of Trickle-Bed Biofilter Media for Toluene Removal; *J. Air & Waste Manage. Assoc.* **1995**, *45* (10), 801-810.
8. Smith, F.L.; Sorial, G.A.; Suidan, M.T.; Breen, A.W.; Biswas, P.; Brenner, R.C. Development of Two Biomass Control Strategies for Extended, Stable Operation of Highly Efficient Biofilters with High Toluene Loadings; *Environ. Sci. Technol.* **1996**, *30* (5), 1744-1751.
9. Delhomenie, M.C.; Bibeau, L.; Gendron, J.; Brzezinski, R.; Heitz, M. A Study of Clogging in a Biofilter Treating Toluene Vapors; *Chem. Eng. J.* **2003**, *94* (3), 211-222.
10. Weber, F.J.; Hartmans, S. Prevention of Clogging in a Biological Trickle-Bed Reactor Removing Toluene from Contaminated Air; *Biotechnol. Bioeng.* **1996**, *50* (1), 91-97.
11. Jorio, H.; Bibeau, L.; Heitz, M. Biofiltration of Air Contaminated by Styrene: Effect of Nitrogen Supply, Gas Flow Rate, and Inlet Concentration; *Environ. Sci. Technol.* **2000**, *34* (9), 1764-1771.
12. Cox, H.H.J.; Deshusses, M.A. Biomass Control in Waste Air Biotrickling Filters by Protozoan Predation; *Biotechnol. Bioeng.* **1999**, *62* (2), 216-224.
13. Fitch, M.W.; England, E.; Zhang, B. 1-Butanol Removal from a Contaminated Airstream under Continuous and Diurnal Loading Conditions; *J. Air & Waste Manage. Assoc.* **2002**, *52* (11), 1288-1297.
14. Konopka, A.; Zakharova, T.; Nakatsu, C. Effect of Starvation Length upon Microbial Activity in a Biomass Recycle Reactor; *J. Ind. Microbiol. Biotechnol.* **2002**, *29* (5), 286-291.
15. Cox, H.H.J.; Deshusses, M.A. Effect of Starvation on the Performance and Re-Acclimation of Biotrickling Filters for Air Pollution Control; *Environ. Sci. Technol.* **2002**, *36* (14), 3069-3073.
16. Mohseni, M.; Allen, D.G. Transient Performance of Biofilters Treating Mixtures of Hydrophilic and Hydrophobic Volatile Organic Compounds; *J. Air & Waste Manage. Assoc.* **1999**, *49* (12), 1434-1441.
17. Sorial, G.A.; Smith, F.L.; Suidan, M.T.; Smith, P.J.; Biswas, P.; Brenner, R.C. Evaluation of Biofilter Media for Treatment of Air Streams Containing VOCs. In *Proceedings of Water Environment Federation 66th Annual Conference and Exposition,* Anaheim, CA, 1993; Vol. 10, pp 429-439.
18. *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; American Public Health Association: Washington, DC, 1995.
19. Zhu, X.; Suidan, M.T.; Alonso, C.; Yu, T.; Kim, B.J.; Kim, B.R. Biofilm Structure and Mass Transfer in a Gas Phase Trickle-Bed Biofilter; *Water Sci. Technol.* **2001**, *43* (1), 285-293.
20. Juneson, C.; Ward, O.P.; Singh, A. Microbial Treatment of a Styrene-Contaminated Air Stream in a Biofilter with High Elimination Capacities; *J. Ind. Microbiol. Biotechnol.* **2001**, *26* (4), 196-202.
21. Smith, F.L.; Sorial, G.A.; Suidan, M.T.; Biswas, P.; Brenner, R.C. Development and Demonstration of an Explicit Lumped-Parameter Biofilter Model and Design Equation Incorporating Monod Kinetics; *J. Air & Waste Manage. Assoc.* **2002**, *52* (2), 208-219.
22. Moe, W.M.; Irvine, R.L. Intracellular Dynamics of Ribonucleic Acid (RNA) and Protein in Microorganisms from Periodically Operated Biofilters; *Water Sci. Technol.* **2001**, *43* (3), 241-248.
23. Webster, T.S.; Cox, H.H.J.; Deshusses, M.A. Resolving Operational and Performance Problems Encountered in the Use of a Pilot/Full-Scale Biotrickling Fiber Reactor; *Environ. Prog.* **1999**, *18* (3), 162-172.
24. Zilli, M.; Palazzi, E.; Sene, L.; Converti, A.; Del Borghi, M. Toluene and Styrene Removal from Air in Biofilters; *Process Biochem.* **2001**, *37* (4), 423-429.
25. Lu, C.Y.; Lin, M.R.; Lin, J.C. Removal of Styrene Vapor from Waste Gases by a Trickle-Bed Air Biofilter; *J. Hazard. Mater.* **2001**, *82* (3), 233-245.
26. Cox, H.H.J.; Moerman, R.E.; vanBaalen, S.; vanHeiningen, W.N.M.; Doddema, H.J.; Harder, W. Performance of a Styrene-Degrading Biofilter Containing the Yeast Exophiala Jeanselmei; *Biotechnol. Bioeng.* **1997**, *53* (3), 259-266.
27. Paca, J.; Koutsky, B.; Maryska, M.; Halecky, M. Styrene Degradation along the Bed Height of Perlite Biofilter; *J. Chem. Technol. Biotechnol.* **2001**, *76* (8), 873-878.
28. Arnold, M.; Reittu, A.; von Wright, A.; Martikainen, P.J.; Suihko, M.L. Bacterial Degradation of Styrene in Waste Gases Using a Peat Filter; *Appl. Microbiol. Biotechnol.* **1997**, *48* (6), 738-744.

**About the Authors**

Daekeun Kim and Zhangli Cai are graduate students and George A. Sorial is an associate professor in the Department of Civil and Environmental Engineering at the University of Cincinnati, Cincinnati, OH 45221-0071. Address correspondence to: George A. Sorial, Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, OH 45221-0071; fax: +1-513-556-2987; e-mail: george.sorial@uc.edu.