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Effect of Carrier Size on the Performance of a Three-Phase Circulating-Bed Biofilm Reactor for Removing Toluene in Gas Stream

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A series of steady-state and short-term experiments on a three-phase circulating-bed biofilm reactor (CBBR) for removing toluene from gas streams were conducted to investigate the effect of macroporous-carrier size (1-mm cubes versus 4-mm cubes, which have the same total surface area) on CBBR performance. Experimental conditions were identical, except for the carrier size. The CBBR with 1-mm carriers (the 1-mm CBBR) overcame the performance limitation observed with the CBBR with 4-mm carriers (the 4-mm CBBR): oxygen depletion inside the biofilm. The 1-mm CBBR consistently had the superior removal efficiencies of toluene and COD, higher than 93% for all, and the advantage was greatest for the highest toluene loading, 0.12 M/m^2-day. The 1-mm carriers achieved superior performance by minimizing the negative effects of oxygen depletion, because they had 4.7 to 6.8 times thinner biofilm depths. The 1-mm carriers continued to provide protection from excess biomass detachment and inhibition from toluene. Finally, the 1-mm CBBR achieved volumetric removal capacities up to 300 times greater than demonstrated by other biofilters treating toluene and related volatile hydrocarbons.

Keywords: Biofilm, circulating-bed, toluene, carrier size, inhibition, oxygen depletion

Among the many water and air pollutants that can be biodegraded aerobically are those whose biodegradation is inhibited by the pollutant itself. Excellent examples are the aromatic hydrocarbons that comprise a major fraction of gasoline: benzene, toluene, and xylenes (BTX). These aromatic hydrocarbons are among the most common contaminants in groundwaters [4, 7, 13, 15, 18], and they also commonly contaminate gases, such as at refineries, during fuel-storage, and with soil-vapor extraction of contaminated groundwaters. Although BTX can be completely biodegraded in aerobic systems, their removal and the growth of BTX-degrading bacteria are seriously slowed by inhibition from BTX themselves [11, 28, 30–33]. If the inhibition is too serious, conventional biological treatment can fail or require large and expensive systems.

Microorganisms that grow very slowly, perhaps due to the inhibition, must be retained in the treatment system with high efficiency. In general, good retention is accentuated when the bacteria are retained as biofilms, which are layer-like aggregates attached to solid surfaces [16]. Biofilm accumulation provides an added benefit when the mass-transport resistance in the biofilm lowers the concentration of the inhibitor inside the biofilm [17].

The three-phase circulating-bed biofilm reactor (CBBR) was developed by Yu and co-workers [11, 28, 30, 31, 33] to treat inhibitory pollutants, and it was extensively tested for BTX removal from contaminated gas streams. In these previous works with the CBBR, the bacteria in the biofilm were retained inside 4-mm cubes of porous cellulose, which is the standard AQUACEL carrier (EcoMat, San Francisco, CA, U.S.A.). AQUACEL carriers are only slightly heavier than water, making them easy to suspend and circulate inside the reactor. The circulation mode of a CBBR precludes clogging of the reactor, or stratification of the biofilm particles.

Yu and co-workers [11, 28, 30, 31] showed conclusively that the internal porosity of the AQUACEL carriers allowed almost all of the biomass to grow inside the

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carrier, instead of on the outside or suspended in the liquid. Being inside the carrier protected the bacteria from detachment and washout, even though the conditions in the liquid phase were highly turbulent. In addition, accumulation inside the carrier set up BTX-concentration gradients, which significantly relieved the inhibition.

Despite the CBBR's success using the standard 4-mm carriers, Yu and co-workers identified a significant limitation: Oxygen depletion inside the biofilm slowed biodegradation rates, particularly the first step of BTX dioxygenation [11, 28, 29, 33]. In our previous study, oxygen limitation was accentuated when the carriers contained more biomass, which resulted from using a higher pollutant-loading rate [19]. In this case, it was possible to have "too much biomass", because additional biomass consumed more oxygen for its endogenous respiration.

The goal of the work presented here was to preclude creating the serious oxygen limitation found with the standard 4-mm AQUACEL carriers because of having too much biomass, while still maintaining the protection role of the porous carriers in biomass retention. To achieve this two-pronged goal, we employed 1-mm AQUACEL carriers, because their smaller size should reduce the buildup of excess biomass, but the internal porosity should maintain the benefits of protection. This study documents that a prototype CBBR using 1-mm porous carriers met the goal for the model compound toluene. The CBBR with 1-mm carriers showed outstanding removal efficiency, stability, and, to our knowledge, by far the highest loading rates obtained by any biological process treating gas-phase BTX.

MATERIALS AND METHODS

The Circulating-Bed Biofilm Reactor

Fig. 1 illustrates the CBBR employed for this study, as well as for Yu and coworkers [28, 30]. The reactor was constructed with glass-tubing segments of 40-mm inner diameter (ID), 8 in. or 4 in. (20.3 or 10.15 cm) long. The working volume was 2.78 l. The nutrient-feeding systems for the reactor included two 8-l nutrient bottles, a 30-l water tank, and pumps, as described in the previous work [11, 28, 30, 31]. The pH in the reactor was 6.8 throughout the experiments. The temperature was maintained at a constant 22°C.

To improve the removal kinetics for the VOCs without harming biofilm accumulation, we selected a smaller AQUACEL carrier size, 1-mm, than the standard 4-mm used before. To achieve a comparable amount of biofilm carrier, we matched the external surface area of the 1-mm carriers to that with the 4-mm carriers used before. The 1-mm (dry) cubes had a side dimension of 1–1.2 mm, an average porosity of 0.93, and a wet density of 1.04 g/cm^3. The average dry weight and wet volume of one of these carriers were 0.13 mg and 1.6 mm^3, respectively.

The toluene-feeding system included compressed house air with an inline air-filter, a flow-meter, a microliter syringe pump, and heating wires, as shown in Fig. 1. The volatile substrate, toluene, was added to the gas flow through a syringe pump, two 10-ml Hamilton gas-tight syringes with size 28 standard thread. The flow rates obtainable were from 0.00728 to 126 µl/min per syringe.

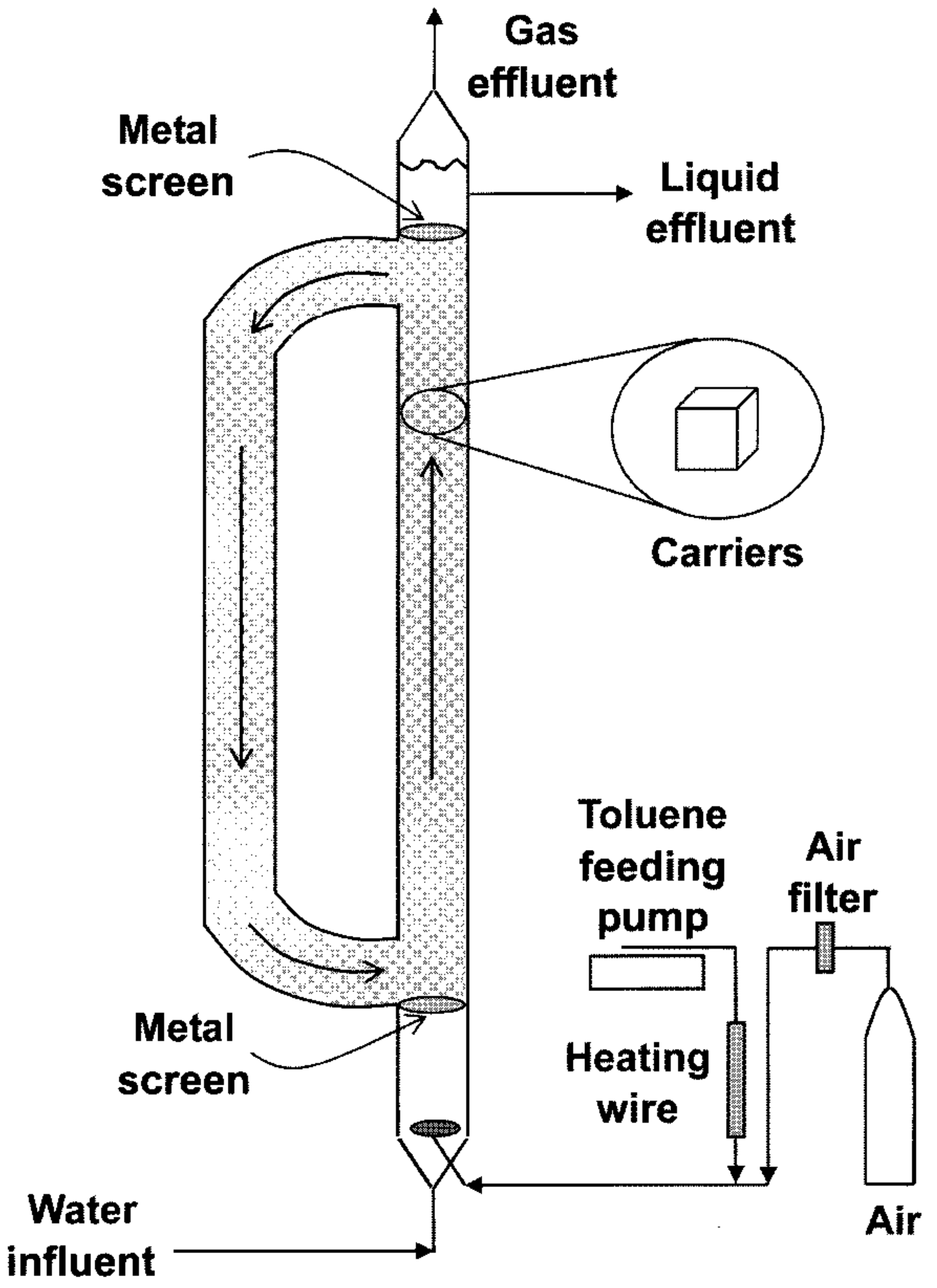

Fig. 1. Schematic of the three-phase circulating-bed biofilm reactor [11, 27, 30].

Each of the 4-in. (10.15-cm) segments in the reactor had two liquid sampling ports. They were sealed with Teflon-faced septa and penetrated by a 12-gauge needle. During sampling, the valve was connected to a gas-tight syringe to withdraw a sample. These ports also could be connected to the dissolved oxygen (DO) probe to measure the DO concentration. Each of the 4-in. (10.15-cm) segments also had one solids-sampling port as described by Yu [28]. This sampling method introduced minimum disturbance to the biofilm, which could otherwise be stripped off the outside of the particles.

Analytical Methods

The amount of biomass in the suspended phase was measured at 540 nm using a Spectronic 21D spectrophotometer (Milton Roy Co., Ivyland, PA, U.S.A.) by its optical density, which was calibrated to dry weight per liquid volume (mg/l). For the porous carrier, biomass was immobilized inside the pores and difficult to remove. Therefore, the biomass in the carriers was measured as the weight difference between the carriers taken from the reactor and clean carriers. Carriers taken from the reactor were first dried at 104°C for 2 h and then weighed immediately.

The COD value measures the oxygen demand equivalent of organic matter that can be oxidized using a strong chemical oxidizing agent (potassium dichromate) in an acidic medium. In this study, standard COD vials of two COD ranges, 0–40 mgCOD/l and 0–150 mgCOD/l, were obtained from HACH Co. (Loveland, CO, U.S.A.).

Table 1. Reactor loading conditions.

Run name	Toluene loading (mol/m^2-day)	
	4-mm carrier[a]	1-mm carrier
Ss1[b]	0.030	0.030
St1-Tol[c]	0.015–0.115	0.015–0.115
Ss2	0.042	0.042
St2-Tol	0.021–0.082	0.015–0.115
Ss3	0.059	0.059
St3-Tol	0.030–0.115	0.015–0.115

*Dissolved oxygen concentration at the gas-liquid interface that was in equilibrium with the oxygen in the gas phase.

[a] Experimental results from Yu and coworkers [11, 27, 29, 30].

[b] Ss indicates the steady-state condition.

[c] St and Tol indicate, respectively, the short-term experiments for a given steady-state condition and that different toluene loadings were used for a constant oxygen loading.

An HP 5890 gas chromatograph (GC) equipped with a flame-ionization detector (FID) and a glass capillary column (Model DB-5; J&W Scientific, Inc., Folsom, CA, U.S.A.) was used to analyze the concentrations of toluene in the gas or liquid phases [28]. The DO (dissolved oxygen) concentration was measured with a high-resolution digital DO meter and probe (Martek Instruments, Inc., Raleigh, NC, U.S.A.; Model Mark XVIII). To measure the DO in the biofilm reactor, the probe was seated in a flow chamber, which was connected to the reactor as described by Yu [28]. The liquid was drawn from the reactor top to minimize the possibility of withdrawing particles and gas bubbles into the DO flow chamber, sent through the chamber containing the DO probe, and then sent back to the reactor.

Toluene-removal Experiments

The CBBR was inoculated with *Pseudomonas putida* F1 obtained from the American Type Culture Collection (ATCC) and also used by Yu and co-workers [11, 28, 30–33]. After *P. putida* F1 was inoculated into CBBR, a few weeks were required to achieve the first steady state.

Because of the protective nature of the porous carriers, biofilm developed rapidly in the carriers. The total flow rate of the liquid influent (nutrient stock solution plus dilution water) was maintained at 42 ml/min, which gave a liquid dilution rate of 22 day^{-1}. The gas flow rate was maintained between 535–540 ml/min, which gave a gas superficial velocity (U_g) of 0.71–0.72 cm/s.

In this study, toluene was the sole electron donor and carbon source. Three steady states were established with air as the gas stream and different toluene loading rates, as shown in Table 1. The toluene loading conditions are identified by the total surface-loading rate. For example, the total surface loading for toluene equaled $r_{pump,T} \times \rho_T / A$, in which $r_{pump,T}$ is the syringe pump's volumetric feeding rate of pure toluene (l^3T^{-1}), ρ_T is the density of toluene ($M_{tol}l^{-3}$) and is known for a given temperature, and A is the total external surface area of the biofilm carriers in the circulating-bed biofilm reactor. For each steady state, a short-term experiment was performed. In the short-term experiments, the gas stream was air, whereas the toluene loading was varied.

To ensure that steady states were reached, the reactor was operated at the first loading until a steady-state condition before the first short-term experiment was conducted. For every other steady state, constant loading was maintained for about 2 weeks. Before the short-term experiments, the gas and liquid effluent qualities were measured for three consecutive days to confirm the steady states. Before each short-term experiment, the toluene loading was changed to a desired value for approximately 3 h. The liquid retention time for CBBR was about 1 h. Therefore, the reactor was sampled after about three liquid retention times. Since the time was too short for the biomass to change dramatically, but long enough for the substrate concentrations to stabilize, short-term experiments were at pseudo-steady states (*i.e.*, the steady states of various toluene loadings with a constant biomass concentration in the reactor). The toluene loading was returned to its steady-state value between each short-term experiment.

We used the same reactor, microbial inoculum, steady-state loading conditions, and experimental protocols as did Yu and co-workers when they documented the performance of the CBBR with 4-mm carriers [11, 28, 30, 31, 33]. The only difference from the prior work is that we used 1-mm porous carriers, instead of 4-mm carriers. Thus, our experimental work directly tested the hypothesis that the smaller biofilm carrier would improve the removal of toluene without sacrificing good biofilm retention.

Format for Presenting the Results

Because our goal is to compare the performance of the CBBR when 1-mm carriers replaced 4-mm carriers, our presentation of the results (Figs. 2–7) matches the format used by Yu and coworkers [11, 28, 30, 31] for the 4-mm carriers. Most of the data are presented with two different sets of results in each figure. One set is for the results of 4-mm carriers, appearing in dashed lines and taken by Yu *et al.* [28, 30, 31], and the second set is for our newly generated results with the 1-mm carriers and appearing in solid lines. In the figures, closed symbols are for the short-term, pseudo-steady-state experiments, and open symbols are for the steady-state conditions.

Two removal efficiencies by the CBBR are calculated. The first is the removal efficiency of toluene based on the toluene entering (gas

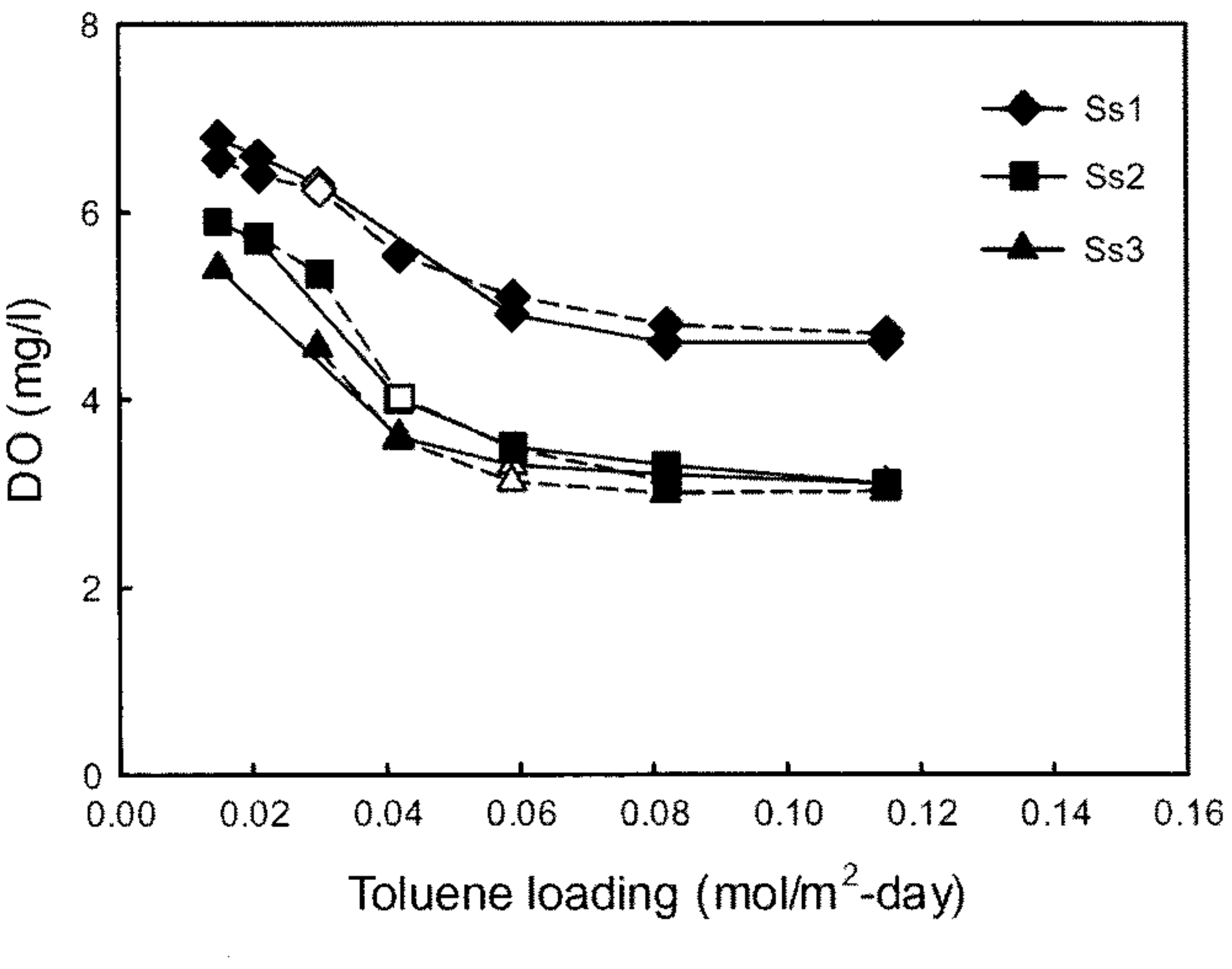

Fig. 2. DO concentrations in bulk liquid of 1-mm and 4-mm CBBRs during Ss1–Ss3.

The open symbols are data from the steady states, and the closed symbols are for their short-term experiments. Only one open symbol appearing for given steady states in 1-mm and 4-mm CBBRs indicates that the values of steady-state conditions are identical. Solid and dashed lines are data from 1-mm and 4-mm CBBRs, respectively.

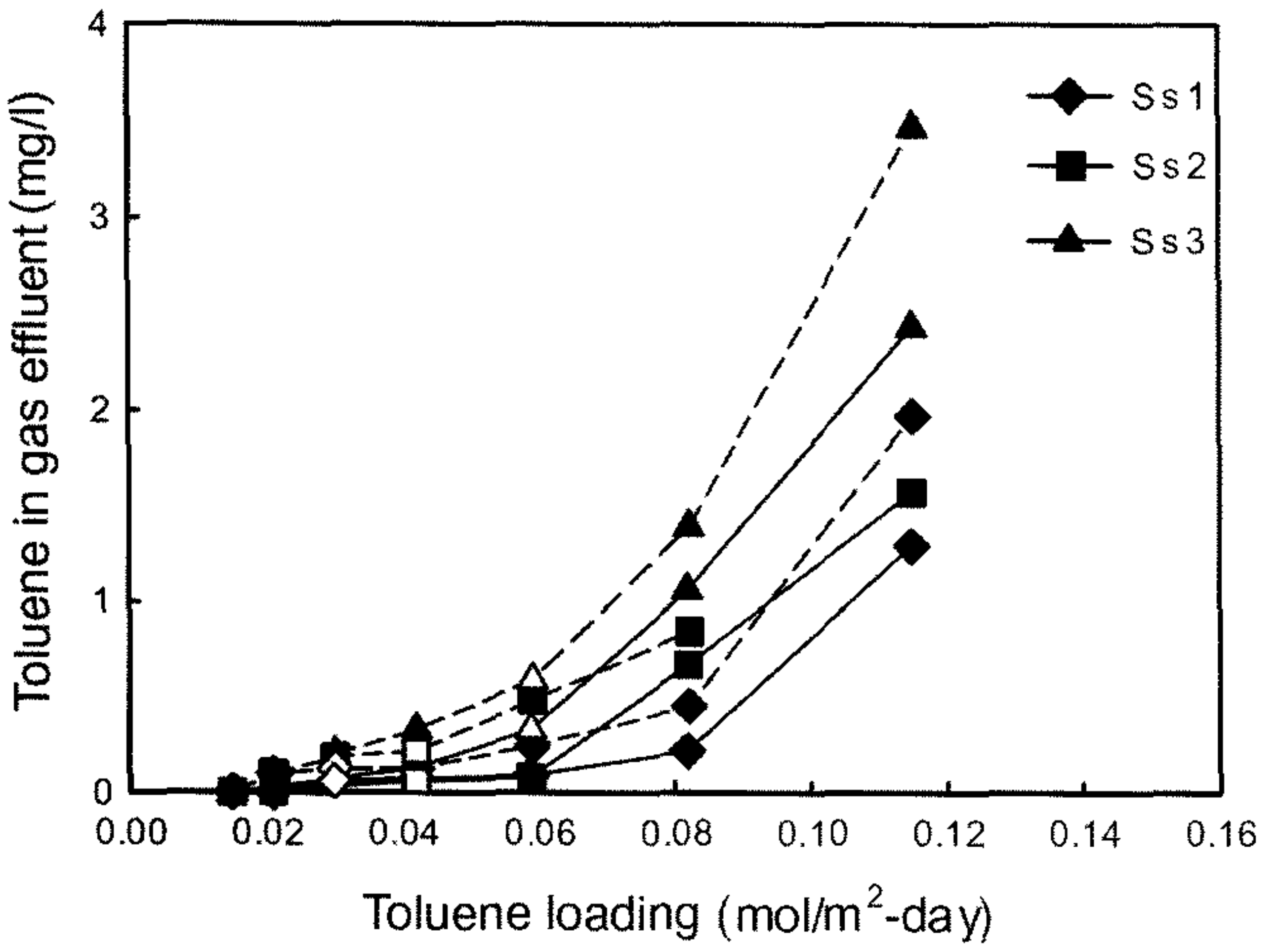

Fig. 3. Toluene concentrations in the gas effluents of 1-mm and 4-mm CBBRs during Ss1–Ss3.

The open symbols are data from the steady states, and the closed symbols are for their short-term experiments. Only one open symbol appearing for given steady states in 1-mm and 4-mm CBBRs indicates that the values of steady-state conditions are identical. Solid and dashed lines are data from 1-mm and 4-mm CBBRs, respectively.

phase) and leaving (gas and liquid phases) the reactor. The second is the removal efficiency of total COD, calculated based on the amount of COD entering (toluene in gas phase) and leaving (toluene in the gas and liquid phases plus intermediates from toluene degradation in the liquid phase) the reactor. The COD in the liquid was measured as the total oxygen demand by toluene, its intermediates, and soluble microbial products [16].

Results and Discussion

Biomass Attached to the Carriers

For each steady state, 50–65 carriers were removed from the CBBR and measured for biomass attached to the carriers. During Ss1, the biofilm concentration in the reactor was 1.8 kg-X_a/m^3-reactor volume, or 1.8 g-X_a/m^2-biofilm surface (Table 2), where g-X_a stands for gram of attached dry weight. With the amount of carriers loaded in this study, the reactor had a specific biofilm surface area of 1,010 m^2/m^3, whereas that for Yu and co-workers [11, 28, 31] was 263 m^2/m^3. The average biofilm density inside the carriers can be calculated from the biofilm dry weight and wet volume of each carrier based on the assumption that the pores were evenly filled with biomass. For example, the average biofilm density was 9.3 mg-X_a/cm^3-carrier during Ss1, and it increased to 16.0 mg-X_a/cm^3-carrier by Ss3. The corresponding densities for the previous work with the 4-mm carriers were 12.0, 16.4, and 23.6 mg-X_a/cm^3-carrier during Ss1, Ss2, and Ss3, respectively.

Although the total biofilm mass in the reactor volume was only slightly larger for the 4-mm carriers, higher biomass per m^2-carrier surface accumulated with the 4-mm carrier. If the biomass accumulated to the same average density in both carriers, the ratio of biofilm depth in 4-mm carrier to 1-mm carrier can be calculated as

$$\frac{L_{f,\,4\text{-mm carrier}}}{L_{f,\,1\text{ mm carrier}}} = 6.8\ (\text{Ss1});\ 4.7\ (\text{Ss2});\ 5.2\ (\text{Ss3}) \qquad (1)$$

where $L_{f,\,4\text{-mm carrier}}$ and $L_{f,\,1\text{-mm carrier}}$ are the biofilm depths in 4-mm and 1-mm carriers, respectively. These results demonstrate that the depth of biofilm in a 1-mm carrier was much thinner than in a 4-mm carrier. This result supports the hypothesis underlying our research with the 1-mm carriers: namely, that diffusion resistance in the biofilm should be reduced by using the smaller carriers. In this case, the average biofilm depth was 4.7 to 6.8 times smaller with the 1-mm carriers.

Table 2 also shows that, as the toluene loading increased from 0.030 mol/m^2-day to 0.059 mol/m^2-day (Ss1 to Ss3),

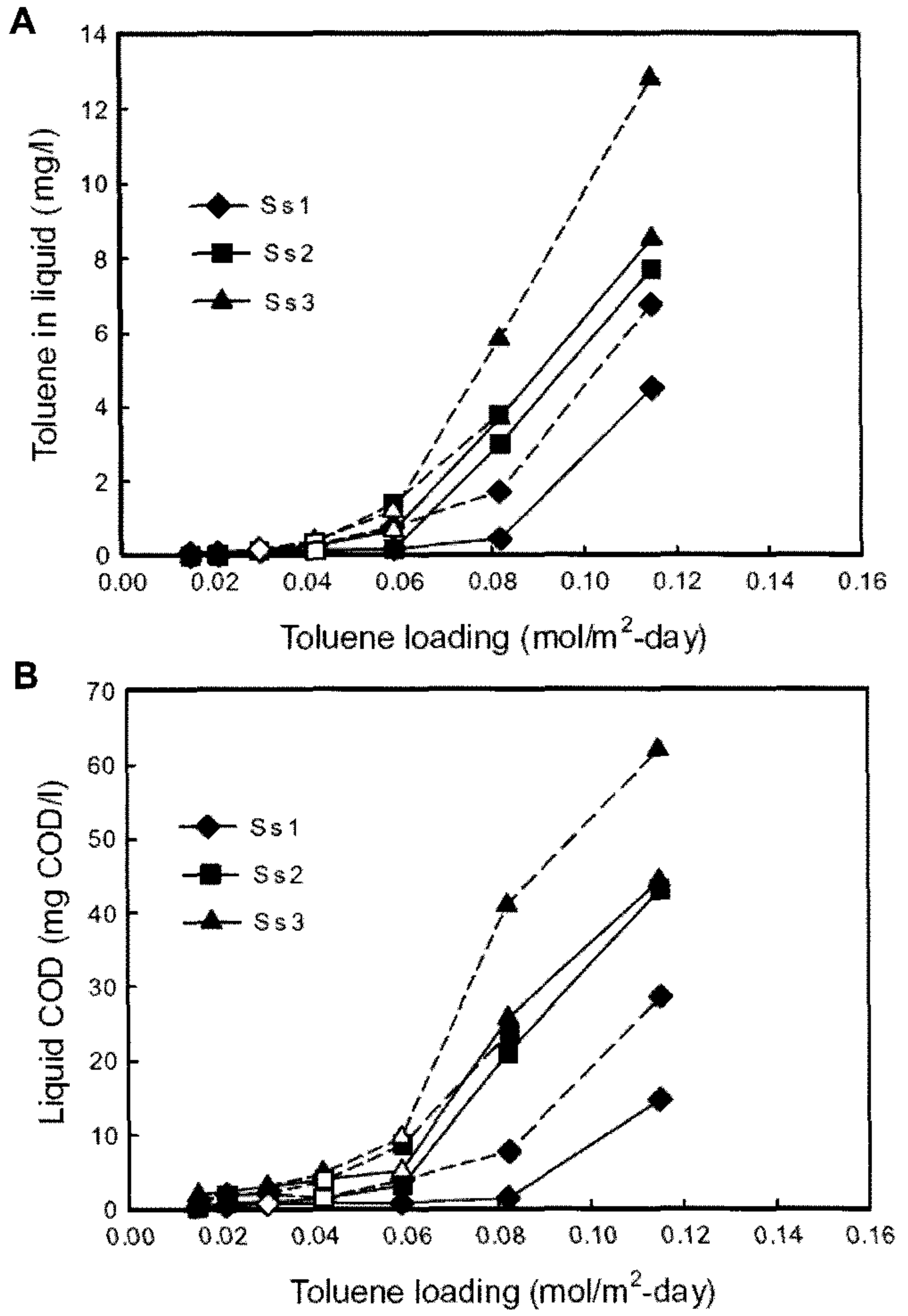

Fig. 4. Toluene (**A**) and COD (**B**) concentrations in bulk liquid of 1-mm and 4-mm CBBRs during Ss1–Ss3.

The open symbols are data from the steady states, and the closed symbols are for their short-term experiments. Only one open symbol appearing for given steady states in 1-mm and 4-mm CBBRs indicates that the values of steady-state conditions are identical. Solid and dashed lines are data from 1-mm and 4-mm CBBRs, respectively.

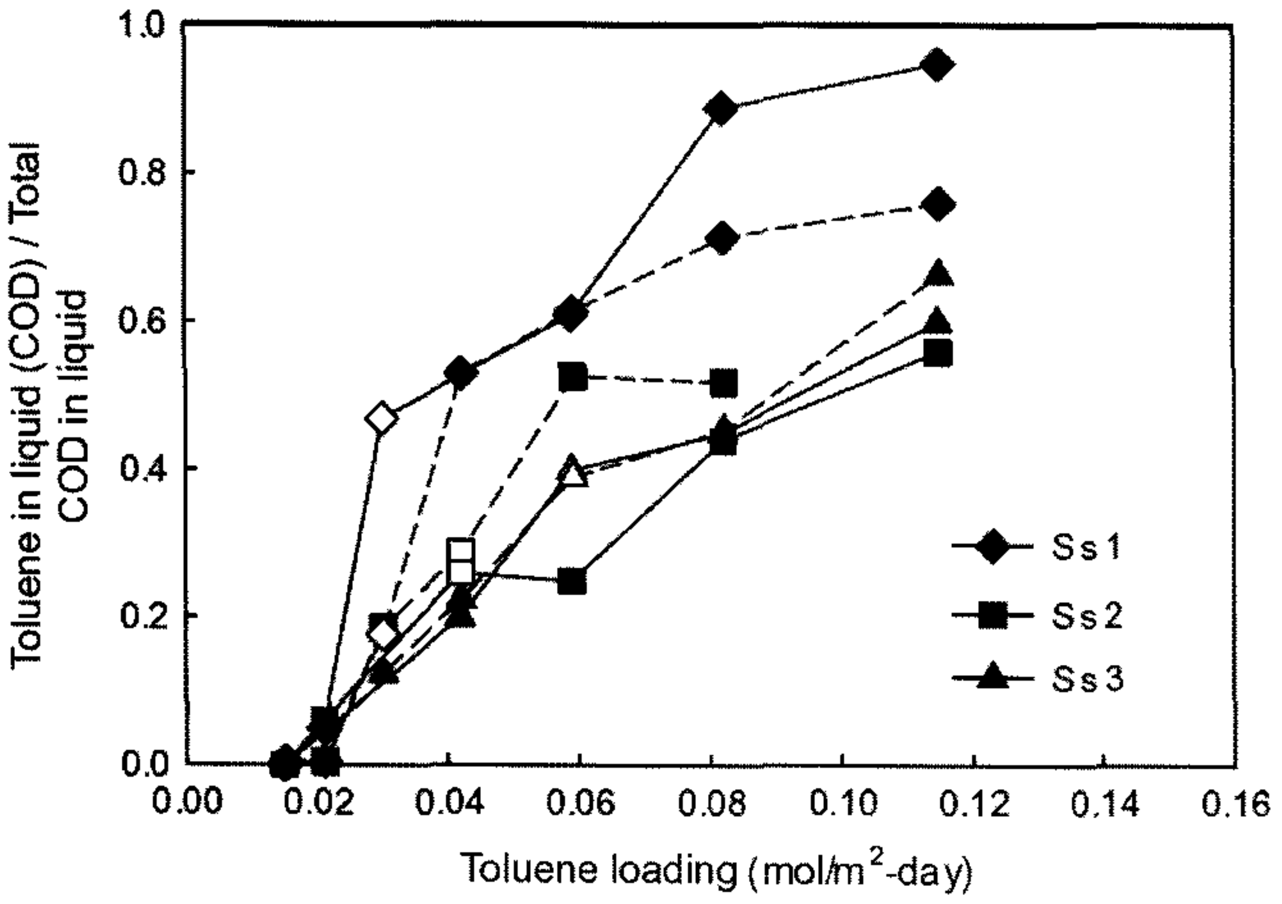

Fig. 5. The fraction of COD that is toluene in the bulk liquid in 1-mm and 4-mm CBBRs during Ss1–Ss3.

The open symbols are data from the steady states, and the closed symbols are for their short-term experiments. Only one open symbol appearing for given steady states in 1-mm and 4-mm CBBRs indicates that the values of steady-state conditions are identical. Solid and dashed lines are data from 1-mm and 4-mm CBBRs, respectively.

the biomass accumulated in the carriers also increased in both CBBRs. Almost all of the biomass was inside the carriers, not on the outer surface. Since the void volume inside each carrier was fixed, a higher substrate loading led to a greater fraction of the carrier voids being filled with biomass.

Biomass in the Suspended Phase

The biomass concentrations in liquid-phase during steady states Ss1-Ss3 and their short-term experiments also are shown in Table 2. The values for each set of experiments for a series varied around a mean. For example, the biomass concentrations during Ss1 fluctuated from 11 mg/l to 25 mg/l, with a mean value of 17 mg/l. The mean value changed systematically, and more biofilm accumulation gave more biomass in the effluent in both CBBRs.

In comparison with the results with the 4-mm carriers [11, 28, 31], the suspended biomass concentrations with the 1-mm carriers were similar to those with the 4-mm carriers. During Ss2 and Ss3, the suspended biomass was lower in the present study (23 *vs.* 28 mg/l for Ss2; 27 *vs.* 36 mg/l for Ss3), although it was higher during Ss1 (17 *vs.* 11 mg/l). The variability in the suspended-biomass concentrations was greater with the 4-mm carriers than with the 1-mm carriers. The fractions of the suspended biomass to the total biomass with the 1-mm carriers were similar, but slightly higher than with the 4-mm carriers: 0.94% *vs.* 0.50% for Ss1, 0.95% *vs.* 0.92% for Ss2, and 0.86% *vs.* 0.85% for Ss3. In summary, the change from 4-mm to 1-mm carriers had minimal impact on the concentration of suspended biomass.

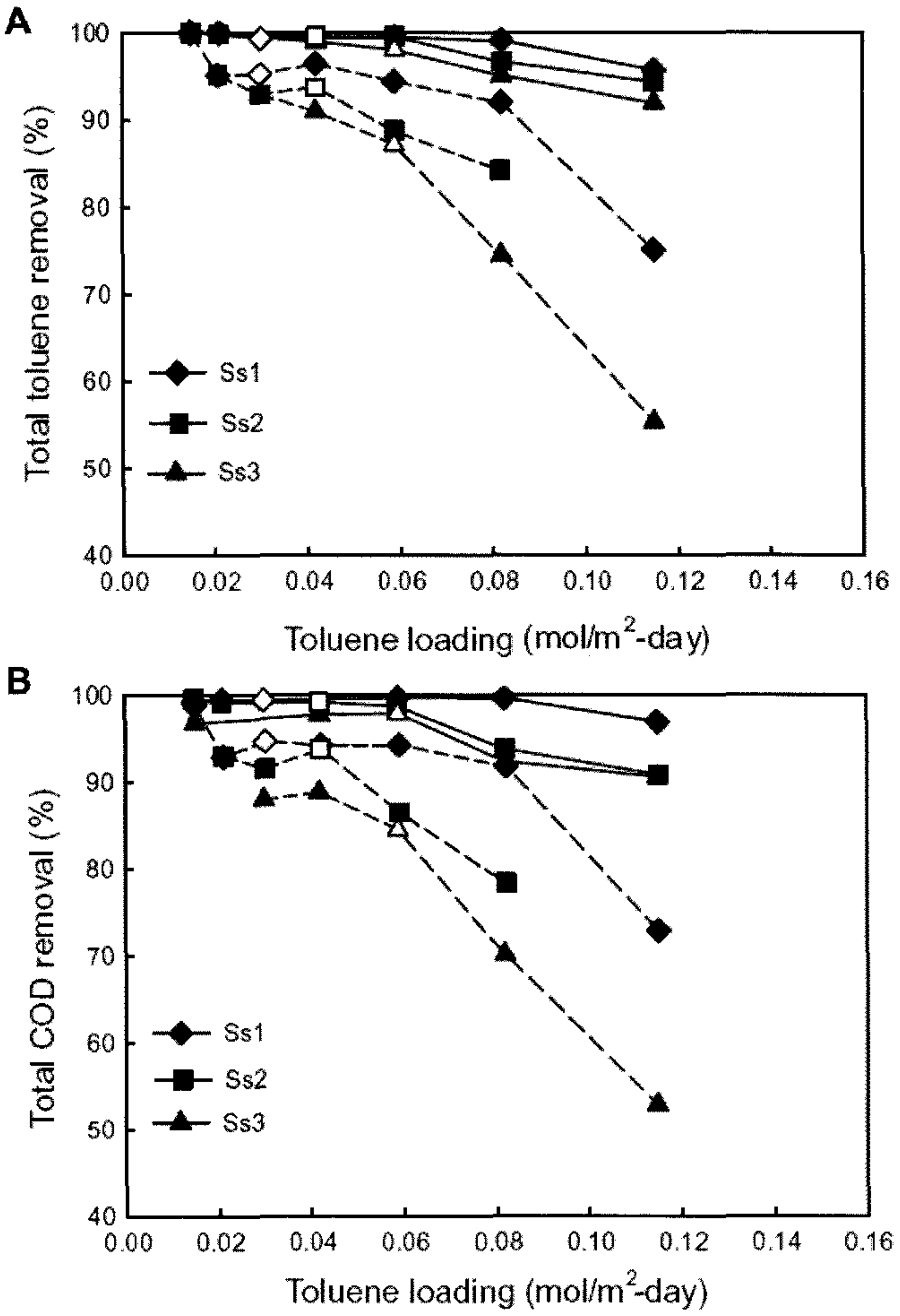

Fig. 6. The percentage toluene (**A**) and COD (**B**) removals in 1-mm and 4-mm CBBRs during Ss1–Ss3.

The open symbols are data from the steady states, and the closed symbols are for their short-term experiments. Only one open symbol appearing for given steady states in 1-mm and 4-mm CBBRs indicates that the values of steady-state conditions are identical. Solid and dashed lines are data from 1-mm and 4-mm CBBRs, respectively.

Influence of Carrier Size on CBBR Performance

Fig. 2 shows the dissolved oxygen (DO) concentrations in the liquid phase during each steady state and the short-term experiments. The DO concentrations were nearly identical for the same surface loading and were not affected by carrier size. As the toluene loading increased for both carriers, the DO concentration decreased steadily and then leveled off in both CBBRs. The leveling implies that the reactor had reached its maximum capacity for oxidizing the toluene. In general, a higher biofilm accumulation (*i.e.*, Ss3>Ss2>Ss1) caused the DO to be lower, and this can be ascribed to more biomass endogenous respiration.

Fig. 3 shows the concentrations of toluene in the gas effluent during Ss1-Ss3 and their short-term experiments. As toluene loading increased, the toluene concentration in the gas effluent increased dramatically in both CBBRs. Lower toluene concentrations in the gas effluent were obtained in

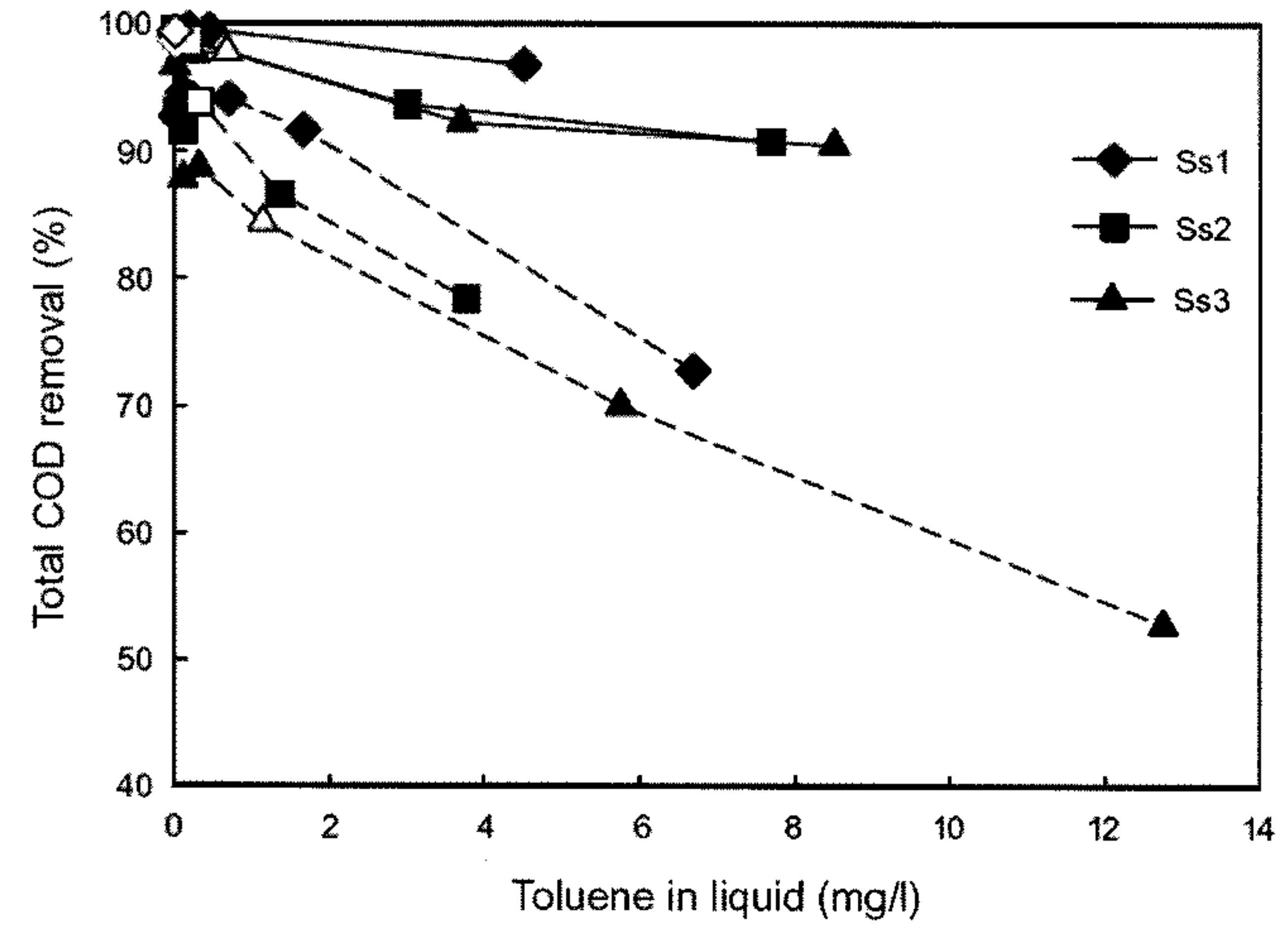

Fig. 7. COD removals at various concentrations of toluene and DO in 1-mm and 4-mm CBBRs during Ss1–Ss3.

The open symbols are data from the steady states, and the closed symbols are for their short-term experiments. Only one open symbol appearing for given steady states in 1-mm and 4-mm CBBRs indicates that the values of steady-state conditions are identical. Solid and dashed lines are data from 1-mm and 4-mm CBBRs, respectively.

the 1-mm CBBR, especially at higher toluene loading. This result is the first evidence that the smaller carriers enhanced treatment performance.

As toluene loading increased among the steady states and in the short-term experiments, the toluene and COD concentrations in the liquid phase also increased, as shown in Fig. 4. The 1-mm carriers had lower toluene and COD concentrations for all experiments, and the advantage was greater with increased toluene loading. These trends further support our hypothesis that the 1-mm CBBR should have superior capacity for toluene removal, in particular for high toluene loading. The impact of carrier size was greater for COD than for toluene, and this shows that the intermediates accumulated substantially less with the 1-mm carrier.

Fig. 5 shows the fraction of the total COD attributed to toluene. In both CBBRs, toluene comprised more of the COD with increased toluene loading for a given steady state. On the other hand, the toluene fraction declined from Ss1 to Ss3 with more biomass available for degradation, *i.e.*, Ss3<Ss2<Ss1. The explanation for both trends is that the increase in toluene loading led to more biomass in the biofilm and suspended phases (Table 2) and to lower DO concentration (Fig. 2). With low dissolved oxygen concentrations, particularly inside the biofilm, the suspended bacteria became relatively more important for toluene dioxygenation, because the suspended bacteria were exposed to the higher DO concentration [19, 30, 31]. The results in Fig. 5 show no systematic advantage for the 1-mm or 4-mm carriers in terms of the toluene fraction. This result reflects that detachment to generate suspended biomass was roughly similar with both carriers (Table 2).

Fig. 6 presents the toluene and total-COD removal efficiencies. In general, toluene-removal efficiencies decreased with increases in toluene loading, but the 1-mm carriers had a significant advantage, especially for high toluene loading. Figure 6 shows that the toluene removal in the Ss3 experiments was less than in the Ss1 experiments, although Ss3 had more biomass in the carriers. This was caused by greater oxygen limitation in the biofilm in Ss3 due to greater endogenous respiration. The 1-mm CBBR showed superior removal efficiency for all loadings, a result that supports our hypothesis that the biofilm inside of a 1-mm carrier did not create as much oxygen depletion as in the

Table 2. Comparison of the results of this study with 1-mm carriers and the previous studies [27, 29, 30] with 4-mm carriers.

Parameter	Steady state	1-mm carriers	4-mm carriers
Biomass attached to the porous carriers ($g\text{-}X_a/l$)	Ss1 Ss2 Ss3	1.8 2.4 3.1	2.2 3.0 4.2
Biofilm-biomass density ($mg\text{-}X_a/cm^3$-carrier)	Ss1 Ss2 Ss3	9.3 12.4 16.0	12.0 16.4 23.6
Biomass in biofilm per m^2-biofilm surface ($g\text{-}X_a/m^2$-biofilm surface)[a]	Ss1 Ss2 Ss3	1.8 2.4 3.1	8.2 11.2 16.1
Suspended bacteria concentration ($mg\text{-}X_a/l$)[b]	Ss1 Ss2 Ss3	17 (11–25) 23 (17–27) 27 (24–32)	11 (7–15) 28 (22–33) 36 (25–44)
Fraction of suspended bacteria to the total bacteria concentration (%)	Ss1 Ss2 Ss3	0.94 0.95 0.86	0.50 0.92 0.85

[a] The biofilm surface for this study was 2.80 m^2 and that for the 4-mm carriers was 0.73 m^2.

[b] Values without parentheses indicate results for each steady state; values in parentheses indicate the range of results including the respective short-term tests.

4-mm carrier for the same toluene loading. For the 1-mm CBBR, over 90% of toluene was removed during all steady states and their short-term experiments. The corresponding values are 85% to 54% for the 4-mm CBBR. The advantages with the 1-mm carrier was most evident for Ss3 and the largest toluene loading, when the impact of oxygen depletion was greatest. The results for percentage COD removal (Fig. 6B) are parallel to those for toluene, although percentage removals were necessarily lower than for toluene.

Fig. 7 shows how the percentage COD removal depended on the directly measured toluene concentration in the bulk liquid. Total COD removal decreased roughly linearly with toluene concentration, and the percentage removal was lower when the biofilm accumulation was greater (Ss3< Ss2<Ss1). Most importantly, the decline of % COD removal was much less for the 1-mm carriers than for the 4-mm carriers.

The biodegradation of toluene is a two-step process: a dioxygenation reaction that produces 3-methyl catechol and does not support the growth of biomass, and a second dioxygenation of the 3-methyl catechol, which leads to products that are oxidized to provide electrons, energy, and carbon for biosynthesis [11, 28, 32, 33]. In this regard, the total COD concentration is of great significance for long-term sustainability of the process. In cases for which intermediates persist, the removal of COD may be the more stringent criterion for assessing reactor performance, because the oxidation of the intermediates provides the electrons, energy, and carbon needed to grow and maintain the biomass. The dioxygenation of 3-methylcatechol requires O_2 as a direct cosubstrate, and it also is inhibited by toluene [31–33]. Mass-transport resistance in the biofilm works favorably to relieve the toluene inhibition, but too much oxygen consumption in the biofilm depletes the O_2 cosubstrate and slows intermediate dioxygenation. The results in Fig. 7 demonstrate that the 1-mm carriers provide a superior balance between relieving toluene inhibition and causing DO limitation. The small biofilm thickness in the 1-mm carrier minimized the adverse effects of DO depletion, while it maintained the benefits of protection from toluene inhibition. Therefore, the CBBR with 1-mm carriers had substantially superior removal of COD (as well as toluene, Fig. 6) for all toluene concentrations.

Performance Comparison of the CBBR for VOCs Removal with other Biofilters

Table 3 summarizes the observed maximum removal capacities of the CBBRs in terms of a volumetric loading rate (*i.e.*, kg/m^3-d or mol/m^3-d). The table also compares the capacities of the CBBRs to many other biofilters used to treat BTX in gas streams. Clearly, the CBBR with 1-mm carriers has the greatest removal capacity based on volumetric loading. Maximum capacity for the 1-mm carriers was about 5 times greater than for the 4-mm carriers. Furthermore, the 1-mm CBBR has a capacity from 2 to 300 times greater than demonstrated by other biofilters.

Although many researchers have demonstrated that biofilters can achieve high removal capacities of volatile

Table 3. Comparison of maximum removal capacities for toluene in a gas stream.

Contaminant	Reactor type	Maximum removal capacity		References
		mol m^{-3} day^{-1}	Kg m^{-3} day^{-1}	
Toluene	Biofilter	5.5	0.507	[14]
Toluene	Biofilter	1.0	0.092	[19]
Toluene	Biofilter	6.5	0.599	[20]
Toluene	Biofilter	3.9	0.359	[2]
Toluene	Biofilter	25.3	2.330	[23]
Toluene	Biofilter	18.2	1.676	[10]
Toluene	Biofilter	43.0	3.960	[8]
Toluene	Biofilter	56.0[a]	5.160[a]	[1]
Toluene	Biofilter	12.3	1.128	[6]
BTX	Biofilter	–	0.064	[22]
BTEX	Biofilter	–	0.044	[9]
Ethylbenzene	Biofilter	0.3	0.027	[2]
Xylenes	Biofilter	0.6	0.066	[8]
Xylenes	Biofilter	13.6	1.440	[2]
Toluene	CBBR with 4-mm cubes	21.0 (Ss1)	1.9 (Ss1)	[27, 30]
		15.3 (Ss2)	1.4 (Ss2)	
		13.4 (Ss3)	1.2 (Ss3)	
Toluene	CBBR with 1-mm cubes	108.0 (Ss1)	10.0 (Ss1)	Present work
		106.1 (Ss2)	9.8 (Ss2)	
		102.7 (Ss3)	9.5 (Ss3)	

[a] Extrapolated values of removal capacity.

pollutants, two common problems with conventional biofilters are an inability to sustain optimal moisture conditions and a tendency to clog with excess biomass during extended use [5, 12, 22, 25–27]. Being a saturated three-phase system, the CBBR is not affected at all by moisture control. The CBBR with macroporous carriers precludes clogging by excessive biomass accumulation, because the biofilm is almost exclusively on the inside of the carriers. Furthermore, the circulating-bed mode of operation prevents bed stratification, a problem that sometimes prevents stable operation of fluidized-bed biofilm reactors. Finally, the CBBR with porous carriers can be used to treat contaminated gases or liquids, since both types of polluted media can be applied to a CBBR. If a contaminated liquid is to be treated, the CBBR must be aerated to provide oxygen and bed circulation.

Experimental results demonstrated that a CBBR with 1-mm porous carriers overcame the performance limitation observed with using 4-mm carriers, but without sacrificing its advantages. First, the 1-mm porous carriers minimized the negative effects of oxygen limitation in the biofilm, because they had 4.7 to 6.8 times thinner biofilm depth. Second, the 1-mm carriers continued to maximize the benefits of outstanding biomass accumulation inside the carrier and protection from toluene inhibition. Because of these characteristics, CBBR with 1-mm carriers showed higher and more stable removal capabilities for toluene and total COD, especially for high toluene loadings. The ultimate result was that the CBBR with 1-mm carriers had the highest volumetric loading capacity demonstrated by biofilters for BTX.

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