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Effects of adsorptive properties of biofilter packing materials on toluene removal

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ABSTRACT

Various adsorptive materials, including granular activated carbon (GAC) and ground tire rubber (GTR), were mixed with compost in biofilters used for treating gaseous toluene, and the effects of the mixtures on the stability of biofilter performance were investigated. A transient loading test demonstrated that a sudden increase in inlet toluene loading was effectively attenuated in the compost/GAC biofilter, which was the most significant advantage of adding adsorptive materials to the biofilter packing media. Under steady conditions with inlet toluene loading rates of 18.8 and 37.5 g/m³/h, both the compost and the compost/GAC biofilters achieved overall toluene removal efficiencies greater than 99%. In the compost/GAC mixture, however, biodegradation activity declined as the GAC mass fraction increased. Because of the low water-holding capacity of GTR, the compost/ground tire mixture did not show a significant improvement in toluene removal efficiency throughout the entire operational period. Furthermore, nitrogen limitations affected system performance in all the biofilters, but an external nitrogen supply resulted in the recovery of the toluene removal efficiency only in the compost biofilter during the test periods. Consequently, the introduction of excessive adsorptive materials in such mixtures should be carefully selected to achieve high and steady biofilter performance.

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1. Introduction

Vapor-phase biofilters have been used successfully in the removal of volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene, xylenes, and styrene emitted from various industrial sources [1-3]. The pollutant-removal processes in biofilters rely on sorption of VOCs followed by biological oxidation in the aqueous, biofilm phase attached to the surface of packing materials. To achieve a stable biofilter performance, therefore, it is important to choose packing materials with appropriate physical and chemical properties, as the surface of the packing materials should allow microorganisms to develop the necessary biofilm structure and should also play a role as a reservoir for moisture, nutrients, and substrate. The preferred characteristics for packing materials used in biofilter applications are: (1) large specific surface area, (2) high porosity, (3) less tendency for compaction, (4) low pressure drop, (5) low cost, (6) high water and nutrient holding capacity, and (7) appropriate adsorbing capacity [4,5].

A number of different packing materials have been studied and employed in biofilter systems for off-gas treatments [4–8], but additional optimization and improvements in efficiency are needed for large-scale applications. Compost is widely used as a packing material because it naturally provides indigenous microorganisms and essential nutrients for microbial growth. On the other hand, compost must be mixed with bulking agents such as wood chips and perlite in order to improve air and water distribution and minimize the compaction of the packing bed.

Because of its ability to adsorb large quantities of target VOCs, granular activated carbon (GAC) can be used as an additive in compost-based biofilters [8]. Furthermore, a biofilter packed with GAC alone has been suggested to treat VOCs [9]. GAC has been used in the treatment of polluted air streams to (1) improve the mass transfer of hydrophobic VOCs from the gas to the biofilm phase, (2) reduce fluctuations in the pollutant concentrations, and (3) enhance the colonization of microorganisms and biofilm formation. Abumaizar et al. [8] used a compost/GAC biofilter to remove a mixture of VOCs in the gas phase, and they reported a higher removal efficiency and stable operation. It has also been reported [10] that a GAC biofilter operated under anaerobic conditions can enhance the removal of tetrachloroethylene. Therefore, combining adsorption and biofiltration processes is believed to be a very promising method for the treatment of recalcitrant compounds. However, a disadvantage in using GAC in biofilters is that the adsorption capacity of activated carbon can be

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substantially reduced by water and microbial growth on its surface [1].

Besides GAC, a number of other adsorptive materials, including natural and synthetic rubbers, have been considered for various applications in environmental engineering systems. Since disposal of waste tires is an environmental problem in many countries, the possibility of recycling tires by using shredded tire strips or ground tire rubber (GTR) in various pollution-preventing applications [11] is an attractive option. GTR has already been used both as a sorption medium in a permeable reactive barrier and as a supplemental aggregate in a slurry cutoff wall for the treatment of VOC-contaminated groundwater [12]. GTR can also be a substitute for activated carbon in liquid-phase biofilters because of its low cost and moderate adsorption capacity for VOCs [13].

The objectives of this study were (1) to investigate the feasibility of mixing different adsorptive materials (i.e., GAC and GTR) with compost, the most common packing material used in vapor-phase biofilters, and (2) to provide guidelines for the selection of suitable packing materials. Additionally, the effects of adsorptive properties and nitrogen availability on biofilter performance were examined. For this study, lab-scale biofilters packed with compost and different adsorptive materials were operated for 70 days each using toluene as a model VOC.

2. Materials and methods

2.1. Packing materials and batch isotherms

The compost used in this study was made from food waste in a composting facility (Saehan Environment Work Co., Seoul, Korea). The compost was sieved through a 2-mm sieve to remove large particles and then sieved through a 1.18-mm sieve to exclude small particles before its use in the biofilters. The GTR was obtained from the Korea Resources Recovery & Reutilization Corporation (Seoul, Korea), and then it was air-dried and passed through a 0.6-mm sieve to obtain uniform particle sizes. The GAC was purchased from an activated carbon company (Samchully Co., Chonan, Korea), and it was also air-dried and passed through a 0.6-mm sieve. The physical and chemical properties of the packing materials used in this study are listed in Table 1.

Batch isotherm tests were performed to determine the packing materials' adsorption capacities for toluene vapor. The packing

 Table 1

 Physical/chemical properties of the packing materials used in this study.

Compost	Bulk density ^a Original water content ^a Water-holding capacity pH Volatile solids ^b Total nitrogen as in TKN Ammonium-nitrogen Nitrate-nitrogen	$\begin{array}{c} 970 \ kg/m^3 \\ 48\% \\ 70\% \\ 8.7 \\ 82.5\% \\ 22,500 \ mg/kg \\ 2390 \pm 80 \ mg/kg \\ 130 \pm 50 \ mg/kg \end{array}$
Granular activated carbon (GAC) ^c	Bulk density Water-holding capacity pH Iodine adsorption BET surface area Total pore volume Average pore diameter	430-480 kg/m ³ 50% 8-10 950 mg/g 950 m ² /g 0.6-0.9 mL/g 16-28 Å
Ground tire rubber (GTR)	Bulk density Specific gravity Water-holding capacity BET surface area	330 kg/m ³ 1.15 5% or less 180 m ² /g

^a Wet weight basis.

^b Dry weight basis.

^c Specification supplied from the producer.

Table 2

The composition of the packing materials and their volume and mass ratios in the mixtures.

Biofilter	Packing materials		
	Compost (g) ^a	Granular activated carbon (GAC) (g) ^b	Ground tire rubber (GTR) (g) ^b
CA (compost alone)	1475	-	-
CG (compost/GAC 1:1)	575	630	-
C2G (compost/GAC 2:1)	705	400	-
C4G (compost/GAC 4:1)	896	225	
CT (compost/GRT 1:1)	529	-	631

^a Wet weight basis.

^b Dry weight basis.

materials were first sterilized by autoclaving, and their moisture contents were adjusted in a range of 50–60%. The batch isotherm tests were then conducted at 20 ± 2 °C by adding two grams of the wet materials and toluene vapor at various gas-phase concentrations into a 40-mL vial equipped with a Mininert[®] screw cap. The vials were shaken in a tumbler at 10 rpm for one day, and headspace gas samples were taken and analyzed periodically.

2.2. Biofilter set-up and operation

Five different mixtures of packing materials were used in the biofilter experiments: (1) compost alone (referred to as "Biofilter CA"), (2) compost and GAC mixture in a volume ratio of 1:1 ("CG"), (3) compost and GAC in a volume ratio of 2:1 ("C2G"), (4) compost and GAC in a volume ratio of 4:1 ("C4G"), and (5) compost and GTR mixture in a volume ratio of 1:1 ("CT"). The biofilter columns were packed with 2.0 L of media at an estimated bulk density of approximately 500 kg/m^3 on a wet weight basis. Table 2 lists the composition and mass ratio of each mixture in each biofilter column. Throughout the biofilter experiments, no attempt was made to inoculate the packing materials with pre-acclimated microbial cultures, so that the toluene biodegradation was carried out by microorganisms that originated from the compost. Because compost naturally contains a wide variety of essential nutrients, external nutrients were not supplied to the packing materials prior to the biofilter experiments.

Each lab-scale biofilter consisted of a 0.3-m-long stainless steel column with an internal diameter of 0.1 m. An airflow generated from a compressor was first passed through an activated carbon filter to eliminate particulates, oil, and residual organics, and then it was split into two streams. A syringe pump (Model 100, KD Scientific, USA) was used to inject research-grade pure toluene into the first air stream, while the second air stream was sparged through a 5-L column filled with distilled water to humidify the air. The two air streams were then combined and introduced into the top of each biofilter column at an air flowrate of 0.09 m³/h, corresponding to an empty bed residence time (EBRT) of 1.6 min. All tubes and connections in the systems were made with stainless steel, Teflon, or glass to minimize toluene adsorption, and the temperature was controlled at 20 ± 2 °C. Prior to the biofilter experiments, the moisture content of filter beds was adjusted to approximately 55% on a wet weight basis. In addition to the humidification of the air stream from the bubble column, 10 mL of water was sprayed over the top of each biofilter column once a day to compensate for the water loss from the bed.

First, a series of experiments (Task I) was conducted using three biofilters packed with the various packing materials (Biofilters CA, CG, and CT) for a 70-day period. On days 0–16 (Phase I of Task I), the biofilters were started at a toluene inlet concentration of 0.5 g/m³ (130 ppm) and an EBRT of 1.6 min, corresponding to an inlet toluene loading of 18.8 g/m³/h. On days 17–27 (Phase II), the inlet toluene concentration introduced to each biofilter was increased to 1.0 g/m³

(260 ppm) at the same gas residence time, corresponding to an inlet toluene loading of 37.5 g/m³/h. On days 28–38 (the transient load period), the inlet toluene loadings subjected to the biofilters were increased from 0.5 to 3.0 g/m³ stepwise in order to determine elimination capacities (ECs). During Phases IV and V (days 39–70), the nitrogen availability and its effect on biofilter performance were examined at the same operating conditions as Phase II. To minimize nitrogen deficiency and to investigate the effect of nitrogen availability on biofilter performance in different packing materials, instead of using the same volume of water, 10 mL/day of 0.1 M KNO₃ solution was added over the top of each biofilter column from day 58 to the end of the operation.

Additional experiments (Task II) using biofilters packed with different mixtures of compost and GAC (Biofilters C2G and C4G) were conducted for 35 days. During these experiments, the same operating conditions as in Phases I and II of Task I were applied to Biofilters C2G and C4G, and the stepwise inlet load increase was also performed for the EC measurements.

2.3. Analytical methods

To determine the overall toluene removal efficiencies and toluene concentration profiles, gas samples were periodically collected from seven sampling ports located along each biofilter column. The gas samples were immediately analyzed using a gas chromatography (600D, Young Lin Instrument Co., Korea) equipped with an HP-FFAP capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$; Agilent, USA) and a flame ionization detector. The pressure drop across each column was measured using an inclined monometer (Dwyer, USA).

Packing materials were withdrawn from three sampling holes located on the sides of the columns and analyzed for moisture content, ammonium, nitrate, and nitrite concentrations. For the moisture content measurements, the media samples were weighed before and after drying at 105 °C. The ammonium samples were prepared by adding two grams of the packing materials to 20 mL of 2 M KCl, and homogenized by shaking vigorously. The ammonium ion concentration was determined by the colorimetric phenate method in accordance with Standard Methods #4500 [14]. For the measurements of NO₃⁻-N and NO₂⁻-N concentrations, two grams of the media samples were extracted with 20 mL of deionized water. The anionic concentrations were determined by an ion chromatography (DX-500, Fa. Dionex GmbH, Germany).

The water-holding capacity of the materials were determined using a procedure known as the 1/3 bar method. The watersaturated sample was placed on a porous ceramic plate and a filter paper (Whatman #2, USA), and 1/3 atmosphere of pressure (about 5 psi) was applied to the bottom of the plate, which forced water out of the sample. The water-holding capacity was determined by comparing the amount of water held in the sample with the dry weight of the sample.

3. Results and discussion

3.1. Abiotic adsorption tests

Prior to the biofilter experiments, the batch isotherm tests were performed to determine the abiotic adsorption capacities of the sterilized packing materials for toluene vapor. Equilibrium concentrations in the gas phase (C_e) and absorbed toluene concentrations in the packing materials (q_e) were used to estimate the Freundlich model coefficients (K_F and N) with a nonlinear best fit method; Table 3 shows the K_F and N estimated for each packing material. The compost showed the lowest adsorption capacity, while the adsorption capacity of the GTR was comparable to that of the compost and significantly lower than that of the GAC.

Table 3

Freundlich model coefficients determined using experimental results from batch isotherm tests for the wet packing materials.

Materials ^a	Number of observations	Freundlic	Freundlich model	
		K _F ^b	Ν	R ²
Wet compost	12	0.34	0.96	0.96
Wet GAC	8	16.1	0.60	0.96
Wet GTR	11	0.87	1.13	0.98

^a The moisture contents were adjusted in a range of 50–60% (wet basis).

^b The unit of K_F is $(mg/kg) (m^3/g)^N$, and the unit of N is dimensionless.

The Freundlich model equation $(q_e = K_F \times C_e^N)$ yields the abiotic toluene adsorption capacities for wet compost, GAC, and GTR of 175, 10620, and 398 mg/kg, respectively, at the equilibrium gas-phase toluene concentration of 0.5 g/m^3 . Using the abiotic adsorption capacities and a simple mass balance, the toluene breakthrough times are predicted to be 0.23, 0.95, and 0.37 days for Biofilters CA, CG, and CT, respectively, when they are operated at the Phase I conditions used in this study. Therefore, it can be expected that the adsorption capacity of the packing materials would have been exhausted within a day in all the biofilters, indicating that the removal of toluene relied primarily on biological degradation after the first day of operations. Still, the adsorptive capacity might be beneficial during the start-up period of the biofilters because, depending on the equilibrium condition, the adsorptive materials could initially adsorb toluene from the gas phase and slowly release the substrate to microorganisms on the surface of packing materials.

3.2. Pseudo-steady-state performance

In the Task I experiments, the three biofilters packed with the different packing materials (Biofilters CA, CG, and CT) were simultaneously operated for 70 days. In Biofilters CA and CG, removal efficiencies greater than 99% were achieved immediately after the start-up and maintained during Phase I, as shown in Fig. 1. The relatively short acclimation period in the compost and the compost/GAC biofilters was presumably due to the presence of indigenous microorganisms capable of actively degrading toluene in the compost. At the comparatively elevated toluene loading condition of Phase II, both Biofilters CA and CG maintained overall removal efficiencies in excess of 99%.

Another interesting finding in this study is that throughout the operational period the compost/ground tire biofilter (Biofilter CT) never achieved high, stable performance, and its removal efficiencies ranged only between 35% and 75%. As mentioned above, the



Fig. 1. Overall toluene removal efficiencies in the lab-scale biofilters packed with compost and different adsorptive materials.

abiotic adsorption capacity of the GTR was much lower than that of the GAC, so the GTR could not have had an appreciably beneficial effect on the mass transfer of toluene. Furthermore, it was difficult to maintain appropriate moisture content in Biofilter CT due to the poor water-holding capacity of the GTR. Severe drying was observed in the entire bed throughout the operational period, even though the inlet air stream was humidified and additional water was supplied directly to the bed on a daily basis to prevent the packing materials from drying. Previous studies have demonstrated that bed drying has a negative effect on microbial activity [15], and a decrease in moisture content from 67% to 30% results in a loss of approximately 50% in toluene removal activity [16]. On day 45, the packing bed of Biofilter CT was thoroughly mixed and adjusted to the optimal water content to address the drying problem, but despite this effort the packing bed remained prone to drying out. Consequently, the ground tire rubber is not a suitable packing material in vapor-phase biofilters, because its water-holding capacity is not sufficient for the growth of microorganisms and it has a negative effect on biodegradation capacity.

3.3. Toluene removal profiles along the columns

During Phases I and II of Biofilters CA and CG, exponential (i.e., first-order) removal of toluene were observed along the biofilter columns, as illustrated in Fig. 2(a) and (b). The compost biofilter (Biofilter CA) achieved active toluene degradation during the initial start-up period (Phase I) and even at the elevated toluene loading condition (Phase II), with greater than 80% of the inlet toluene being degraded in the first 5 cm of bed depth (see Fig. 2(a)). In contrast, for the biofilter packed with compost/GAC 1:1 (Biofilter CG, see Fig. 2(b)), a longer inlet zone of the biofilter column was required to complete the biodegradation of toluene introduced during the initial start-up period. When the inlet toluene concentration increased in Biofilter CG (days 17–27), the toluene removal profile even shifted up along the column.

For comparison, a series of biofilter operation (Task II) was conducted for 35 days with compost/GAC mixtures at different ratios (Biofilters C2G and C4G). As with the experimental results obtained from the biofilter operations in Task I, both Biofilters C2G and C4G achieved overall removal efficiencies greater than 99% at the operating conditions of Phases I and II. Furthermore, exponential removals of toluene along the biofilter columns were observed (data not shown), implying that indigenous microorganisms originating from the compost actively degraded toluene mostly in the inlet zone of the biofilters. The toluene removal profiles also shifted up at the elevated toluene loading condition during the same period of the Biofilters C2G and C4G operation.

An equation for first-order toluene removal along the length of the column was applied to fit the experimental data:

$$C_{\rm g} = C_{\rm g,in} \times \exp(-k_1 x), \tag{1}$$

where C_g is the gas-phase toluene concentration (ppm), k_1 is the first-order removal coefficient (cm⁻¹), and x is the distance from the inlet (cm). A simple data-fitting method yielded the first-order removal coefficients for the operating conditions with different packing materials, as listed in Table 4. The compost/GTR mixture showed the lowest first-order degradation coefficient in the Phases I and II conditions. The estimated toluene removal coefficients for Biofilter CA were high and similar to those of Biofilter C4G. As the compost fraction in the compost/GAC mixture decreased (i.e., C4G \rightarrow C2G \rightarrow CG), the estimated first-order removal coefficients decreased correspondingly, indicting that a longer inlet zone of the biofilter column was required to completely biodegrade the substrate when a higher mass fraction of the GAC was mixed with the compost.



Fig. 2. Toluene concentration profiles along the column length for Biofilters (a) CA, (b) CG, and (c) CT.

The pollutant-removal profiles along the biofilter columns and their changes with operational time can be used as an indicator of biofilter performance [3]. In this study, the differences in the removal profiles and the estimated removal coefficients imply that the local biodegradation rate near the column inlet was substantially lower in the compost/GAC 1:1 (Biofilter CG) than in the

Table 4

Estimated first-order removal coefficients that yielded best fits to the experimental results.

Biofilter	Phase I condition ^a (cm ⁻¹)	Phase II condition ^b (cm ⁻¹)
CA (compost alone)	0.31	0.31
CG (compost/GAC 1:1)	0.16	0.14
C2G (compost/GAC 2:1)	0.29	0.18
C4G (compost/GAC 4:1)	0.35	0.30
CT (compost/GRT 1:1)	0.05	0.04

^a The inlet toluene concentration of 0.5 g/m^3 and an EBRT of 1.6 min.

 $^{\rm b}\,$ The inlet toluene concentration of 1.0 g/m 3 and an EBRT of 1.6 min.

compost alone column (Biofilter CA). Furthermore, the removal coefficients of toluene removal indicate that the biodegradation activity of Biofilter C2G was slightly higher than that of Biofilter CG but lower than that of Biofilter C4G. As a result, when the toluene inlet loading was stable and low (i.e., lower than 40 g/m³/h at the condition herein), the biodegradation activity decreased when the GAC fraction in the mixture was increased. This may have been because the GAC used in this study was less suitable for the growth of indigenous microorganisms that originated from the compost at the given pseudo-steady-state conditions, or it may have been due to localized nutrient limitations, as discussed further below.

3.4. Effect of water and nitrogen supply

Following the pseudo-steady-state and dynamic-load periods, the three biofilters (CA, CG, and CT) were continuously operated for additional 30 days at the same operating condition as in Phase II. Over this additional period of operation, the biofilter performance gradually deteriorated (Phase IV, see Fig. 1). This decrease in biofilter performance was also evident in the toluene degradation profiles determined along the biofilter columns (Fig. 2). The toluene removal profiles for both Biofilters CA and CG shifted to an almost flat and linear shape along the columns, indicating a loss of biodegradation activity.

Possible reasons for the decline in the biofilter performance include compaction of the filter bed, excessive microbial growth, inappropriate water content, and nutrient limitation. Since the measured pressure drop ranged from 0.5 to 0.8 cm of water across the columns throughout the entire period of biofilter operation, the activity decline could not be due to severe compaction and excessive microbial growth. As mentioned earlier, severe drying was observed in the compost/ground tire media. In Biofilters CA and CG, however, the average moisture content of the packing materials determined on day 50 was 68%, implying that the moisture content was not the primary reason for the decline of biofilter performance.

Of all the nutrients, nitrogen makes up the largest fraction of microorganisms (about 12% for a typical bacterial cell formula of C₅H₇O₂N) and is essential for sustaining microbial growth and activity [17]. The form of nitrogen utilized is also important as microorganisms will uptake readily available inorganic nitrogen sources such as NH₄⁺ and NO₃⁻. When the nitrogen demand for microbial activity exceeds the nitrogen available in packing media, the operating conditions become nitrogen limited, and a decline in biofilter performance is generally observed [17,18]. Gribbins and Loehr [19] reported that a media nitrogen level of 1000 mg/kg was required in a compost biofilter to remove toluene effectively. On day 50, biofilter media were sampled from the top, middle, and bottom levels of the biofilter columns to test whether nutrient limitation were affecting the toluene removal efficiency. As shown in Tables 1 and 5, the average concentration of available nitrogen (i.e., NH_4^+ – N and NO_3^- – N) along the CA biofilter column declined from an original value of 2520 to 396 mg/kg on day 50. In all the biofilters, the readily available nitrogen concentrations determined on day 50 were much lower than the threshold value; we believe that these low levels were the main reason for the decline in the toluene degrading efficiencies in the compost and compost/GAC biofilters.

Besides the averaged nitrogen concentration, the localized concentrations of available nitrogen along with the biofilter columns (data presented in Table 3) also affected the shifting of toluene removal profiles into the columns and the decline in the biofilters' overall performance. In all of the biofilters, the concentration of available nitrogen was lower at the top (inlet) of the columns than at the bottom (outlet) of the columns when measured on day 50. The shifting of the toluene removal profiles further into the columns (Fig. 2, differences between data for days 17–27 and days 39–57) is entirely consistent with the gradual development of local kinetic

Table 5

Concentrations of available nitrogen in the packing materials on day 50.

Biofilter	Level	NH ₄ -N (mg/kg)	NO ₃ -N (mg/kg)	Total available nitrogen (mg/kg)
CA (compost alone)	Top ^a Middle ^b	269 252	62 122	331 374
	Bottom ^c	287	195	482
	Тор	136	26	162
CG (compost/GAC 1:1)	Middle	146	47	193
	Bottom	149	70	219
	Тор	118	32	150
CT (compost/GTR 1:1)	Middle	147	70	217
	Bottom	140	71	212

*Nitrite = not detected.

^a Top section = 0-10 cm.

^b Middle section = 10–20 cm.

^c Bottom section = 20–30 cm.

limitations due to the lack of nitrogen availability. Furthermore, the fastest toluene degradation was observed near the outlet of the CG Biofilter during days 39–57 (Fig. 2(b)), which is consistent with previous studies conducted using inert packing materials, where the location of the localized kinetic limitation was shifted further into the column as a function of time [18,20]. In addition, the toluene removal profiles shifted quickly as the mass fraction of GAC in the packing media increased or as the amount of nitrogen available in the columns at the beginning of the experiment decreased. Consequently, biofilter designers and operators should take the averaged and localized nitrogen availability into account when incorporating adsorptive media without adding externally supplied nutrients.

To minimize the nitrogen deficiency and to investigate the effect of nitrogen availability in different packing materials on biofilter performance, 10 mL/day of 0.1 M KNO₃ solution was added to the three biofilters from day 58 until the end of the experiment (Phase V). The removal efficiency of Biofilter CA was slowly restored and reached approximately 95% at the end of the operation. In contrast, the removal efficiency of Biofilter CG was not substantially improved (see Fig. 1) until the end of the operation, even though an identical nitrogen source was externally supplied to the media. As shown in Table 5, the soluble nitrogen concentration in the compost/GAC media was lower than that in the compost biofilter because of the nitrogen sources would have been required to improve the performance of Biofilter CG. Furthermore, this study clearly demonstrated that more evaluations are



Fig. 3. Elimination capacities (ECs) for toluene. The EC values were determined on days 28–38 at various inlet loading rates.

needed to determine an optimal nitrogen range in biofilters when the adsorptive materials need to be mixed with compost.

3.5. Effect of adsorptive properties

The major advantage of adding adsorptive materials to packing media is likely to be the enhanced buffering capacity of the biofilters to different unsteady loadings. In this study, the transient responses of the biofilters to dynamic inlet loadings such as step and pulse inputs were investigated. First, the biofilters were subjected to step increases in the inlet toluene concentration, which is commonly known as the elimination capacity (EC) test in vapor-phase biofilter literature. EC tests are typically performed by sequentially increasing the inlet pollutant loading stepwise and calculating the EC corresponding to each pollutant loading



Fig. 4. Transient responses to a pulse input in Biofilters (a) CA, (b) CG, and (c) CT.

[21]. In this study, the inlet toluene loading was increased from 0.5 to 3.0 g/m³ stepwise on days 28-38. Each loading condition was maintained for more than 24h to obtain guasi-steady-state responses of the biofilters, and the corresponding EC value was calculated. Of the packing mixtures tested, Biofilter CT yielded the lowest maximum EC of approximately $41 \text{ g/m}^3/\text{h}$ in spite of its moderate adsorptive capacity (see Fig. 3). The highest maximum EC was $101 \text{ g/m}^3/\text{h}$ at a toluene loading rate of $115 \text{ g/m}^3/\text{h}$, observed in both Biofilters C4G and C2G, which implies that the adsorptive capacity of the GAC improved the performance of the biofilter when subjected to the sequential loading changes. However, as illustrated in Fig. 3, the EC lines determined in Biofilters C4G and C2G did not substantially differ from those of Biofilters CG and CA in the moderate loading range. These findings clearly indicate that, to enhance biofilter performance, biodegradation activity should be balanced with adsorptive capacity in the packing materials.

As another dynamic inlet loading experiment, the pulse input of toluene (about a five-fold increase from its baseline concentration for two hours) was introduced to the biofilters, and the gas-phase concentrations in the inlet (\bullet in Fig. 4), the middle point (\Box), and the outlet (\mathbf{v}) of the columns were monitored. As Fig. 4(a) illustrates, the toluene concentrations, determined in the middle and the outlet of Biofilter CA, rapidly increased and closely reflected the pulse input due to its low adsorptive capacity. The removal efficiency of the compost biofilter at the pulse input condition was only 30%, and it required almost three hours to restore the previous steady-state condition when the toluene input was switched back to the baseline concentration. In contrast, in Biofilter CG, no substantial changes in the toluene concentrations determined in the middle and the outlet of the column were observed during the pulse input test. In addition, a re-acclimation time was not required in Biofilter CG after the decrease in the input loading, implying that the adsorbed toluene was subsequently degraded by microorganisms. The compost/ground tire biofilter showed an overall removal efficiency of 73% during the pulse input and showed some extent of retardation of toluene. However, the amount of toluene removed from the first half of the column was dramatically reduced due to its minimal adsorption capacity, and approximately three hours were required to return to the previous state after the toluene concentration was brought back to the baseline. Similar to other experimental findings reported in the literature [8,9], the adsorption capacity of activated carbon as a packing material can have a beneficial effect by leading to a more stable performance of biofilters operated under shock loading conditions.

4. Conclusions

This study was conducted to investigate the effects of different adsorptive materials on biofilter performance. The packing materials tested in this study included: (1) compost alone, (2) mixtures of compost and GAC, and (3) a mixture of compost and GRT. The key observations and specific conclusions that can be drawn from this research are as follows:

 Under the steady loading conditions, both compost and compost/GAC biofilters showed high toluene removal efficiencies and active biodegradation, mostly in the front half of the column. However, biodegradation activity declined in the compost/GAC mixture as the GAC mass fraction increased. Meanwhile, no significant improvement in the biofilter performance was observed for the compost/GRT mixture throughout the entire operational period because not only the mixture had a low toluene adsorption capacity but also it was difficult to maintain the moisture content in the optimal range.

- 2. During the short-term pulse tests, a sudden increase in the toluene loading was effectively attenuated in the compost/GAC biofilter, while a rapid toluene breakthrough and slow reacclimation were observed in the compost biofilter at identical loading conditions. Therefore, a mixture consisting of compost and adsorptive materials can be a feasible alternative to conventional biofilters, particularly when the biofilter systems experience dynamic loading changes.
- 3. Because of limitations in the amount of available nitrogen, toluene degradation activity gradually declined after a month of operation in the compost and compost/GAC biofilters. The addition of an external nitrogen source resulted in the recovery of the toluene removal efficiency in the compost column, while the removal efficiency of the compost/GAC biofilter was not immediately improved. These experimental findings indicate that it is difficult for biofilters packed with the adsorptive materials to achieve stable VOC removal performance due to the low moisture and nutrient holding capacities of the materials.

Overall, this study presented herein suggests that, in order to improve biofilter performance, it is important to balance biodegradation activity with adsorption capacity when determining the mixture of packing materials. Additional studies need to be performed to suggest the optimal ratio of adsorptive materials in such mixtures. Finally, achieving stable biofilter performance over extended periods will require more research into the best ways to maximize microbial activity through controlling the microenvironments, including moisture content and nutrient availability.

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