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Impact of interchanging VOCs on the performance of trickle bed air biofilter

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Abstract

Trickle bed air biofilters (TBABs) were evaluated under conditions of an interchange of the feed volatile organic compounds (VOCs). Two aromatic compounds (toluene and styrene) and two oxygenated compounds (methyl ethyl ketone and methyl isobutyl ketone) were interchanged as single solutes. The results obtained revealed that the biofilter provided high removal efficiency within the critical loading, which was previously defined in the non-interchanging VOC-fed biofilters. The biofilter recovered easily to the 99% removal after interchanging to oxygenated compounds, regardless of the immediately preceding compound fed to each biofilter, but for aromatic compounds, a longer reacclimation period was required. The biofilter response after interchange of feed VOCs depended on the physicochemical property of feed VOCs as well as the biomass retained in the biofilter prior to interchanging VOC. Using high EBRT at the critical loading (which corresponds to high inlet concentration), problems related to oxygen limitation within the biofilm may have appeared. It was noticed that a smaller ratio of COD/N and a larger ratio of CO_2/COD were encountered after an interchange of the feed VOCs.

Keywords: Trickle bed air biofilter; Interchanging VOC; Empty bed retention time; Reacclimation

1. Introduction

Biological treatments are operated best on steady loads of the contaminant. However, variations in contaminant load are common in real applications. The biological solids in a plug-flow reactor can not effectively withstand shock loads as compared to a completely mixed reactor because the incoming contaminant is dispersed uniformly in the latter reactor. Biofilters for VOC control in gaseous waste streams are hydraulically very similar to plug-flow reactors.

It is worthwhile noting that biofilters operating in industry are exposed to a spectrum of changing conditions, particularly when they are assigned to the treatment of waste air for discontinuous processes. In chemical industries, the most common variation in the waste air composition is weekly rotation in production. For example, a solvent manufacturing industry continues producing a specific solvent depending on demand for a specific period of days. From this point of view, a number of studies have been devoted towards biofiltration under dynamically varying loading conditions, e.g., variable air flow rate and contaminant concentration, or periodical shut down of contaminants [1–4]. To our best knowledge, the effects of dynamic change of feed contaminants on biofilter performance have not been fully understood yet. Also, knowledge about the biofilter performance in adjusting to the new compound needs to be known in advance of a real application.

In general, microbial ecosystems are able to respond in a very dynamic manner to changes in their environment, particularly to changes that stress the community [5]. However, the greater the variability of substances to be controlled, the greater are the constraints placed on the ability of the biofilter to control VOCs. When VOCs with different physiochemical properties are treated by rotation in a biofilter, the empty bed residence time (EBRT) can be the most important factor in controlling the biofilter performance. In previous studies by the authors [1,6], biofilter performance for single VOC removal was optimized. It was found that aromatic compounds required longer EBRTs to be utilized than the oxygenated

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compounds. In general, biofilter performance depends on EBRT. Numerous studies [7–10] reported that an increase of the gas flow rate provides an inverse effect on the elimination capacity and removal efficiency in the biofilter. The response to gas flow rate can be due to the decrease in the contact time between the pollutant and the microbial population, and also a result of the physicochemical properties of the VOCs.

In the present study, the impact of interchanging VOCs as dynamic feeding conditions on the biofilter performance was explored by using two independent parallel lab-scale trickle-bed air biofilters (TBABs). As the empty bed residence time (EBRT) was expected to be the most critical parameter in the condition of interchanging feed VOCs, the biofilters were operated at different EBRTs. One had constant EBRT and the other had various controlled EBRTs corresponding to stable removal efficiency obtained in a previous study [1]. The interdependence between biofilter performance and nitrogen utilization and CO_2 production was investigated as well.

2. Materials and methods

2.1. Selection of VOCs

The experimental work was performed on two independent parallel-train lab-scale TBABs under the interchange of the feed VOCs. Two aromatic compounds (toluene and styrene – dimensionless Henry's law constants 0.280 and 0.109 at 25 °C, respectively [11]) and two oxygenated compounds (methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) – dimensionless Henry's law constants 0.00194 and 0.00062 at 25 °C, respectively [11]) were employed in this study. The VOCs of concern are common solvents employed in the industry and are major components of paints and varnishes.

2.2. Reactor design

The biofilters were constructed of seven cylindrical glass sections with an internal diameter of 76 mm and a total length of 130 cm. A head space section and a bottom section were designed for the inlet of VOC-containing air and buffered nutrient solution, and for the outlet of treated air and leachate, respectively. Each biofilter was packed with pelletized diatomaceous earth biological support media (Celite® 6 mm R-635 Bio-Catalyst Carrier, Celite Corp., Lompoc, CA) to a depth of about 60 cm. Detailed descriptions of the physical properties of the media are found elsewhere in the literature [12]. The biofilters were maintained at a constant operating temperature of 20 °C in a constant temperature chamber. Operations of the biofilters were conducted in a co-current gas and liquid downward flow mode.

The purified air supplied to the biofilters was treated for removal of water, oil, carbon dioxide, VOCs, and particles by a Balston FTIR purge gas generator. The air flow to the biofilters was regulated by a mass flow controller set up at the desired value. Liquid VOC was injected via a syringe pump into the air stream where it vaporized, and entered the biofilters. The biofilters were equipped with an independent system for feeding 1.5 L/day (default value) of a buffered nutrient solution. The feed was sprayed as a fine mist onto the top of the bed media through a spray nozzle. The buffered nutrient solution consisted of deionized and activated carbon filtered water, and a mixture formulated to contain all necessary macronutrients, micronutrients, and buffers, as described in a previous study [13]. Nitrate was used as the sole source of nutrient-nitrogen because the use of nitrate instead of ammonia can be effective in reducing the observed biomass yield and provides better performance of biofilters [12]. The nutrient formulation for the biofilters contained the same amount of nutrient-nitrogen and phosphorus ratio of a given VOC loading (a COD-to nitrogen ratio of 50:1 and a nitrogen-to-phosphorous ratio of 4:1).

2.3. Biofilter operation

The biofilters continued to be run, without reconditioning the media used in previous runs, where styrene (namely, Biofilter "A") [6] and MIBK (namely, Biofilter "B") [14] had been the sole VOC contaminants. The feed VOCs were stepwise interchanged in the sequence of aromatic compounds and oxygenated compounds or the reverse order. The inlet VOC concentrations were varied from 50 ppmv to the maximum allowable concentration, which was determined to be the corresponding critical loading obtained in a previous study [1]. The critical loadings were 3.52, 1.90, 5.63 and 3.26 kg COD/m^3 day for toluene, styrene, MEK, and MIBK, respectively. In order to evaluate the biofilter performance under different EBRTs, biofilter "A" was run at a constant EBRT of 2.02 min. This EBRT corresponds to a stable biofilter performance for 99% removal of styrene [6]. The operation of biofilter "B" was conducted at different EBRTs for each feed VOC. These EBRTs correspond to the stable biofilter performance for 99% removal of each VOC [1]. The conditions for this study are summarized in Table 1.

Since a coordinated biomass control strategy is unavoidable to attain consistent high removal efficiency of the biofilter, the biomass control strategy for this study involved a periodic in situ up-flow washing with the nutrient solution, i.e., backwashing, at a rate of 1 h a week during the experimental period. The details of the backwashing methodology are described elsewhere in other studies [6,12,13].

2.4. Analytical methods

Gas phase samples for VOC analysis were taken with a gas-tight syringe. These VOC concentrations were measured by using a gas chromatography (GC) (HP 5890, Series II, Hewlett Packard, Palo Alto, CA) equipped with a flame ionization detector, and a 30 m narrow bore column (DB 624, J&W Scientific, Folsom, CA). Effluent gas phase samples for

Table 1
Experimental conditions for this study

	Stage I	Stage II	Stage III	Stage IV	Stage V
Biofilter "A"					
Feed VOC	Styrene	MEK	Toluene	MIBK	Styrene
Inlet concentration (ppmv)	200	50–1075	50–400	50–400	200
Loading rate (kg COD/m^3 day)	1.90	0.26–5.63	0.43–3.52	0.40–3.26	1.90
(g/m^3 h)	(25.8)	(4.4–96.1)	(5.7–46.9)	(6.1–49.9)	(25.8)
EBRT (min)	2.02	2.02	2.02	2.02	2.02
Biofilter "B"					
Feed VOC	MIBK	Toluene	MEK	Styrene	MIBK
Inlet concentration (ppmv)	150	50–250	200–400	50–200	150
Loading rate (kg COD/m^3 day)	3.26	0.7–3.52	2.8–5.63	0.47–1.90	3.26
(g/m^3 h)	(49.9)	(9.3–46.9)	(47.8–96.1)	(6.4–25.8)	(49.9)
EBRT (min)	0.76	1.23	0.76	2.02	0.76

CO_2 analysis were also taken by using gas-tight syringes. A GC equipped with a thermal conductivity detector was used for determining the CO_2 concentration. Liquid phase samples were analyzed for nitrate, total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. Nitrate was determined by using a UV–vis spectrophotometer (Shimadzu UV mini 1240 UV–vis spectrophotometer) at a wave length of 220 nm. TC and IC were determined by using a TOC analyzer (Shimadzu TOC 5000 analyzer). The VSS concentration in the effluent and backwashing solution were determined, according to Standard Methods 2540 G [15].

3. Results and discussion

3.1. Overall performance

The performance of biofilter "A" and biofilter "B" with respect to VOC removal is shown in Figs. 1 and 2, respectively. Since the VOCs were fed within the critical loading capacity, high removal performances were apparently achieved for both biofilters during the experimental period.

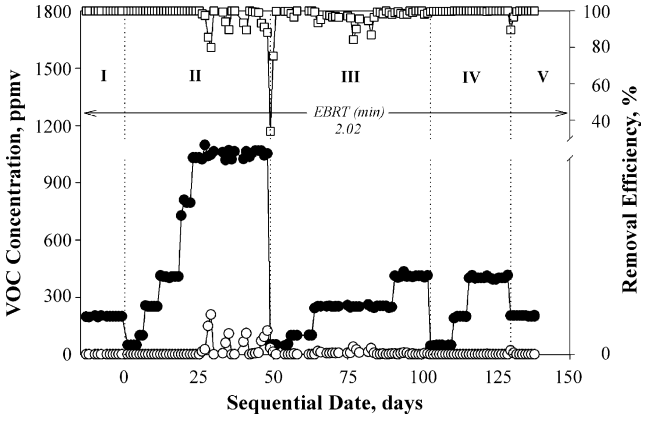

Fig. 1. Performance of biofilter "A" as a function of feed VOCs at a constant EBRT of 2.02 min. (I) Styrene, (II) MEK, (III) Toluene, (IV) MIBK and (V) Styrene. (□) Removal efficiency (%); (●) Inlet concentration (ppmv) and (○) Outlet concentration (ppmv).

3.1.1. Biofilter "A"

Biofilter "A" was run at a constant EBRT of 2.02 min. The feed VOCs were interchanged in the sequence of styrene, followed by MEK, toluene, MIBK, and finally styrene. Operation stage I was the last 15 days in a previous study [6], in which the styrene was fed at a loading rate of 1.90 kg COD/m^3 day with a corresponding inlet styrene concentration of 200 ppmv. Stage II was conducted with MEK, which was fed within the critical loading rate of 5.63 kg COD/m^3 day. However, at an inlet MEK concentration of 1075 ppmv the removal efficiency dropped to as low as 80% prior to backwashing. In the biofiltration of MEK as sole contaminant, over 99% removal performance was observed at this loading rate [16], but the corresponding inlet concentration was 400 ppmv at 0.76 EBRT. It can be speculated that at the high inlet concentration in the current study, the biofilter performance might have deteriorated due to oxygen limitations within the biofilm. Yang et al. [17] also demonstrated that at the high VOC inlet concentration, limitation of nutrients or oxygen in the biofilm can cause deterioration in the biofilter performance.

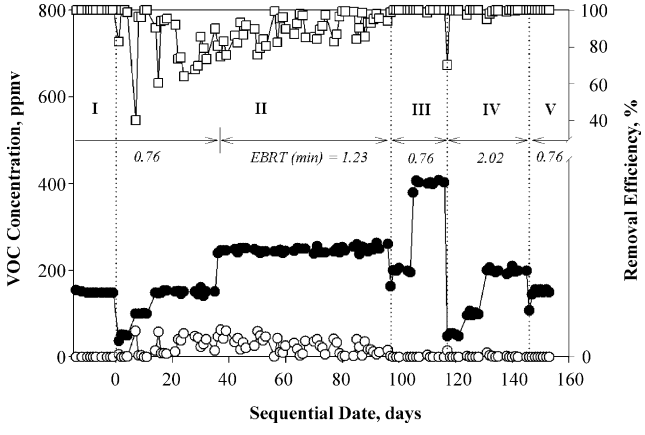

Fig. 2. Performance of biofilter "B" as a function of feed VOCs at a different EBRTs. (corresponding to the stable biofilter performance for 99% removal of each VOC in previous study [1]): (I) MIBK, (II) Toluene, (III) MEK, (IV) Styrene and (V) MIBK. (□) Removal efficiency (%); (●) Inlet concentration (ppmv) and (○) Outlet concentration (ppmv).

During stage III, MEK was interchanged with toluene. At 250 ppmv inlet toluene concentration, the removal efficiency decreased to 85% on day 77 and day 83 prior to the backwashing. In order to improve the desired high removal efficiency by increasing the nitrogen diffusion driving force [6,18], the inlet molar flow of the nitrate-nitrogen in the liquid nutrient was increased to 44 mmol/day on day 83. On the third day, the overall removal efficiency was over 99% and remained at this level. When MIBK was fed (Stage IV), the biofilter provided a consistent high removal performance within the critical load. Finally, styrene was introduced into the biofilter at the critical loading rate and 99% removal performance was attained. Fig. 1 illustrates the time course of the experiment for biofilter "A".

3.1.2. Biofilter "B"

The feed VOCs were interchanged in the sequence of MIBK, followed by toluene, MEK, styrene, and finally MIBK. The unit was started up at 150 ppmv MIBK and a 0.76 EBRT with a corresponding loading rate of 3.26 kg COD/m^3 day (stage I represents the last 15 days in a previous study [14]). At an EBRT of 0.76 min, toluene was fed up to and within the critical loading rate of 3.52 kg COD/m^3 day. At low inlet concentrations of 50 and 100 ppmv, 99% removal efficiency was attained after slightly greater than one day of reacclimation. However, at higher inlet concentrations of 150 and 250 ppmv the removal efficiencies initially dropped below 85%. On day 27, the inlet molar flow of the nitrate-nitrogen in the liquid nutrient was increased to 44 mmol/day in order to be equivalent to that of biofilter "A". But, the removal efficiency still remained below 85%. It has been noted by other researchers that large gas flow rate can have an adverse effect on the removal efficiency of a biofilter [10]. Thus, on day 37 the EBRT was increased to 1.23 min, c.f., 2.02 min in biofilter "A". By day 44, the removal efficiency gradually increased to about 94%. On day 50 when backwashing was conducted, 2243 g VSS/m^3 of biomass was washed out. Consequently, the removal efficiency dropped to as low as 75% before regaining the 99% level on day 55. In a previous study by the authors [19], about 1305 g VSS/m^3 of biomass was removed through backwashing at the same conditions as the present study, but a constant removal efficiency was attained. From the results of the two studies taken together it appears that much longer reacclimation after backwashing was involved in the current study due to removal of too great an amount of accumulated biomass. By day 96, the removal efficiency was over 99%, but it decreased to about 85% prior to backwashing, which could be a result of mass transfer limitation as the available surface was reduced by biomass accumulation. On day 97, stage III was started up with MEK. The removal efficiency remained stable at the 99% level up to 5.63 kg COD/m^3 day. After interchanging the feed VOC to styrene (stage IV), the removal efficiency initially dropped to 70%, but rose to 99% in 20 h, and remained at that level. Finally, MIBK was fed into the biofilter at the critical loading rate of 3.26 kg COD/m^3 day and the removal efficiency was measured at over 99%. Fig. 2 illustrates the time course of the experiment for biofilter "B".

3.2. Biofilter response after an interchange of feed VOCs

In order to investigate the initial response of each biofilter after an interchange of feed VOCs, effluent samples were collected at prescheduled time intervals to evaluate the biofilter response. Reacclimation period was considered to have been achieved when 99% of the original biofilter performance was attained. The results obtained are presented in Fig. 3. It is observed that MEK and MIBK had much better biofilter recovery immediately after VOC interchange as compared to the other two VOCs (styrene and toluene). In general, it was seen that the biofilter recovered to 99% – removal within 30 min after interchanging to MEK and MIBK, regardless of the previous VOC. However, the reacclimation period for toluene and styrene removal was delayed for both biofilters "A" and "B". It is common that microorganisms exposed to a new substrate may require a period of acclimation before they begin vital degradation. Furthermore, it is speculated that biofilter response after interchange of feed VOCs depends on the physicochemical properties of interchanged VOC as well as the biomass accumulated in the biofilter.

Regarding the physicochemical properties of a VOC, it is worthwhile noting that the response of a microbial community to a new substrate is different according to the chemical structure of substrate [20]. The toxicity of the substrate to a microbial community is dependent on its concentration. Materials that are toxic to one species may enhance the metabolism in another or may have no effect [21]. In this study, it was found experimentally that oxygenated compounds, e.g., MEK and MIBK, were utilized as a new substrate without any retardation in removal efficiency, while aromatic compounds, e.g., toluene and styrene, needed a relatively longer reacclimation period. In general, metabolism of aromatic compounds is more complicated as compared

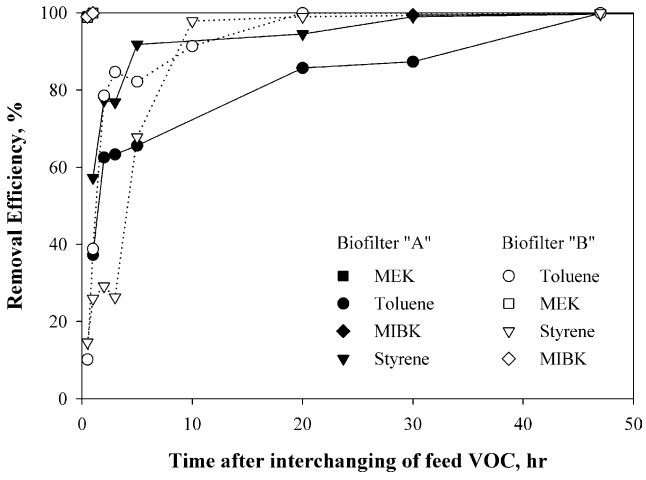

Fig. 3. Effluent response corresponding to interchange of feed VOCs. Symbols for MEK and MIBK are shown only at 0.5 and 1 h due to their fast recovery in biofilter performance.

to that of oxygenated compounds [21]. Aerobic biodegradation of an aromatic compound involves two steps: activation of the ring involving the incorporation of molecular oxygen into the ring, and ring cleavage involving the cleavage of the bond between carbon atoms of the two hydroxyl groups [22].

It appears from Fig. 3 that with respect to toluene, biofilter "B" recovered to a 99% removal efficiency more rapidly than biofilter "A". But, as seen in Figs. 1 and 2, consistently high toluene removal was not observed in biofilter "B" as compared with biofilter "A". As mentioned previously, toluene removal in biofilter "B" could have been impacted by the biomass accumulated in the biofilter prior to toluene feeding, details of which are provided in Section 3.5. It is possible that since in biofilter "A" the organisms were first acclimated to styrene the enzymes or microorganisms that effectively open the ring were present in the biofilm even after being fed MEK, whereas in biofilter "B" the microorganisms present had only been provided MIBK prior to introduction of toluene. Thus only a limited population of organisms may have been present in the biofilm that could initially produce the appropriate enzymes to degrade toluene. Addition of nitrogen was required to increase their population. Thus the shorter EBRT in biofilter "B" coupled with a biofilm predominately consisting of MIBK-degrading organisms together with the differing physicochemical properties of toluene could have resulted in relatively poor mass transfer, accounting for the relatively unsteady behavior observed as toluene concentrations were increased. For styrene, no definitive conclusion can be drawn since an equal EBRT was used in both biofilters, and in Biofilter "B", by the time styrene was fed to the bed, toluene-degraders had a chance to colonize it.

3.3. Concentration profiles in the biofilters

To evaluate biofilter performance and to determine the removal rate constant at the critical loading for each feed VOC, gas samples were taken along the media depth of the biofilter one day following backwashing. The data are expressed as the cumulative EBRT (within the media bed) and plotted using a semi-logarithmic scale for the residual concentration in order to observe if the first-order removal rates are satisfactory approximations to the biokinetics, and to determine the value of the related rate constants (see Fig. 4). Linear regression analysis was used to obtain the first-order removal rate constants. Table 2 provides the first-order removal rate constants together with sum of the square of the residuals (R^2). The removal rate constant for MEK in biofilter "A" is unexpectedly much lower than that for biofilter "B" and has low R square values. It should be noted that in order to obtain a critical loading of 5.63 kg COD/m^3 day at 2.02 min EBRT for biofilter "A", an inlet concentration of 1075 ppmv MEK was used. It is hypothesized that at high concentration of a substrate, zero order kinetics might better describe the substrate degradation than first order kinetics. In fact, if one develops the zero order rate constant for MEK in biofilter "A", it is found that a rate constant of 0.027 g/m^3 s was obtained with 0.96 R^2. This strongly suggests that a decrease in the removal rate was caused by the high inlet concentration. Furthermore, if one considers a Monod kinetics formulation, a first-order relation is obtained at low substrate concentration and then changes to a zero-order relation at high substrate concentration [20].

Table 2
Reaction rate at critical load for feed VOCs

VOC	Biofilter "A"			Biofilter "B"		
	EBRT (min)	Rate constant (s^{-1})	R^2	EBRT (min)	Rate constant (s^{-1})	R^2
Toluene	2.02	0.021	0.97	1.23	0.035	0.93
Styrene	2.02	0.044	0.97	2.02	0.043	0.95
MEK	2.02	0.038	0.84	0.76	0.107	0.94
MIBK	2.02	0.063	0.99	0.76	0.098	0.94

It can be seen in Table 2 that the removal rate constants in biofilter "B" are larger than those in biofilter "A" for all VOCs studied except for styrene. Contrary to this observation, low EBRT generally results in an adverse effect on the biofilter performance [7–10] due to insufficient contact time between the substrate and the biofilm. In this study, it should

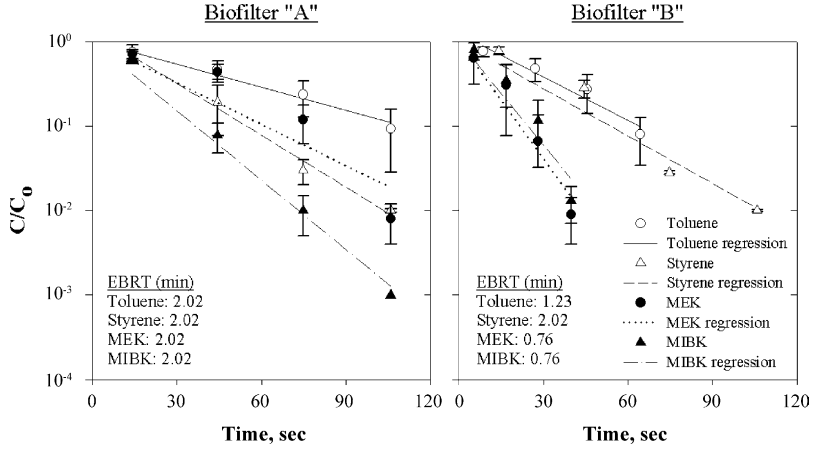

Fig. 4. Reaction rate as a function of feed VOCs and EBRT. Kinetic constants were determined at critical load for each feed VOC assuming first-order kinetics.

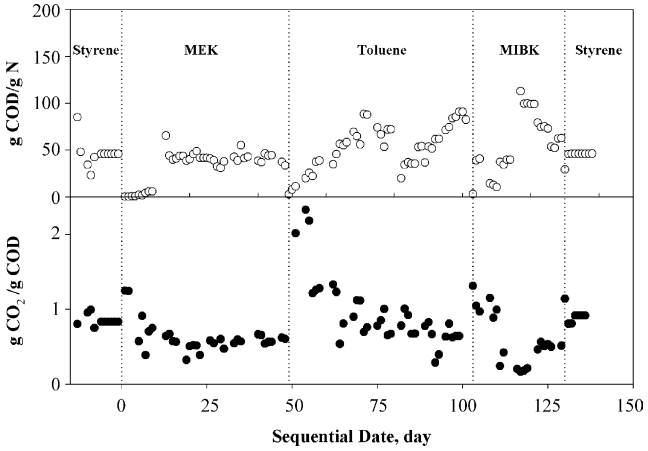

Fig. 5. Nitrogen utilization and CO_2 production (Biofilter "A").

be noted that in order to maintain the same loading rate for each biofilter, the influent concentration of the VOC of concern was adjusted, according to the EBRT employed. Hence at the critical loading for each VOC studied, the influent concentration in biofilter "A" was higher than that in biofilter "B" except for styrene. On the other hand, the depth of the biofilter media that was utilized was similar for both biofilters (see Fig. 4) regardless of the EBRT. These results suggest that if the loading rate is to be maintained constant and within the critical loading rate for each VOC, the overall biofilter performance is dependent on the influent concentration of the feed VOC, or correspondingly by the oxygen-demand.

3.4. Nitrogen utilization and CO_2 production

Analyses for influent and effluent concentration of nitrate and CO_2 concentration in each biofilter were conducted. Fig. 5 shows the ratios of COD/N and CO_2/COD against the sequential date for biofilter "A". A similar behavior of nitrogen utilization and CO_2 evolution was also observed in biofilter "B" (data are not presented). In Fig. 5, significant changes are shown after interchanging VOCs during the experimental periods. One possible explanation for this is that, after feeding other substrates, a series of biochemical changes will occur for acclimation of a microbial community to the new substrate; for example, in order to begin using the compound for food, the genes must create the transfer RNA, which then produced the proteins that make up the enzymes for utilizing the new substrate [23]. Greater utilization of nitrogen for producing the RNA or enzymes/proteins might then occur, but that would not explain the evolution of CO_2 as shown in Fig. 5. Another possible explanation is that other microorganisms such as facultative organisms contributed to this behavior, or that respiration and/or death of some of the microbial community that is no longer able to degrade the new substrate takes place accounting for the evolution of CO_2. For example, denitrifying microorganisms are generally facultative [22]. Zhu et al. [24] observed microorganisms associated with known denitrifying organisms in trickle bed biofilters which treated toluene, *n*-hexane, diethyl ether, and butanol as single substrates. It was demonstrated in their study that NO_3^- can serve as a major electron acceptor responsible for the degradation of significant portion of a treated VOC, specifically with an extremely low Henry's constant. du Plessis et al. [25] also found significant denitrification activity in an aerobic biofilter for toluene removal. In the study of the degradation of aromatic hydrocarbons in saturated soil under mixed electron acceptor conditions [26], it was confirmed that facultative denitrification can occur in the presence of both oxygen and nitrogen.

On the other hand, since the specific growth rate tends to increase with an increase in the substrate concentration as predicted by a Monod-type relationship [21], the step-increase in the VOC concentration would affect the trends of g COD/g N initially. However, the observed trends of g CO_2 /g COD are not fully explained by this line of reasoning.

To better interpret the experimental data, further investigation of microbial communities is needed. DGGE analysis of PCR-amplified 16S-rDNA fragment for each feed VOC would provide further understanding of the microbial community structure and diversity within the biofilm, but was beyond the scope of the current study.

3.5. Carbon balance and nitrogen balance

Both carbon and the nitrogen balances were conducted during all experimental periods. Table 3 shows that the carbon recoveries for the two biofilters were similar. It is speculated that the unaccounted carbon contributed to the biomass retained within the biofilter. In the case of nitrogen recovery, the unaccounted nitrogen was 22.8 and 12.5% for biofilter "A" and biofilter "B", respectively. The loss of nitrogen from both biofilters might be explained if it served as the main electron acceptor in the reactor [24].

Carbon recovery during the experimental period of each feed VOC is also developed in Fig. 6. Bars indicate carbon recovery for a single VOC in the feeding sequence. Each bar includes the carbon equivalent of CO_2 produced in the effluent gas, the carbon equivalent of VSS (biomass) in the effluent liquid and the backwashing liquid, inorganic carbon in the effluent liquid, and total organic carbon in the effluent liquid. It is seen from Fig. 6 that carbon recovery was underestimated for oxygenated compounds, e.g., MEK and MIBK, while in the case of toluene and styrene, carbon was over estimated in three out of four cases. Assuming that the unaccounted carbon in the carbon balance contributes to the accumulation of biomass in the biofilter, oxygenated compounds were degraded easily and deposited additional cell mass in the biofilter. However, in the case of the removal of aromatic compounds, biomass release overwhelmed biomass accumulation which is consistent with a cell population die off and growth of new biomass. The result is consistent with and confirms our earlier suggestion in Section 3.2 that the amount of biomass retained in the biofilter affected biofilter reacclimation after interchanging the feed VOC. The esti-

Table 3
Carbon recovery[a] and nitrogen recovery[b]

	Carbon recovery (%)					Nitrogen recovery (%)		
	$^{a}C_{CO2}$	$^{b}C_{VSS}$	$^{c}C_{IC}$	$^{d}C_{TOC}$	$C_{unaccounted}$	^{e}N	$^{f}N^{c}$	$N_{unaccounted}$
Biofilter "A"	63.2	20.0	0.8	1.8	14.2	45.2	32.0	22.8
Biofilter "B"	63.1	19.7	0.7	1.0	15.5	48.9	38.6	12.5

[a] Carbon balance: $C_{VOC\ removed} = {}^{a}C_{CO2\ in\ effluent\ gas} + {}^{b}C_{VSS\ in\ effluent\ liquid\ and\ backwashing\ solution} + {}^{c}C_{Inorganic\ carbon\ in\ effluent\ liquid} + {}^{d}C_{Total\ organic\ carbon\ in\ effluent\ liquid} + C_{Biomass\ retained\ in\ the\ reactor}$. A typical cellular composition for a heterogeneous microorganism can be represented as $C_5H_7O_2N$.
[b] Nitrogen balance: assuming that N utilization is independent of loading, $N_{Nitrogen\ utilized} = N_{nitrogen\ used\ for\ biomass\ growth} + N_{nitrogen\ serve\ as\ electron\ acceptor}$. Since the net accumulation of attached biomass in the reactor is not equal to be zero, $N_{nitrogen\ used\ for\ biomass\ growth} = {}^{e}N_{VSS\ in\ effluent\ liquid\ and\ backwashing\ solution} + {}^{f}N_{Biomass\ retained\ in\ the\ reactor}$.
[c] Estimated from $C_{unaccounted}$ in an assumption that the carbon unaccounted in the experiment is equal to the carbon retained in the reactor.

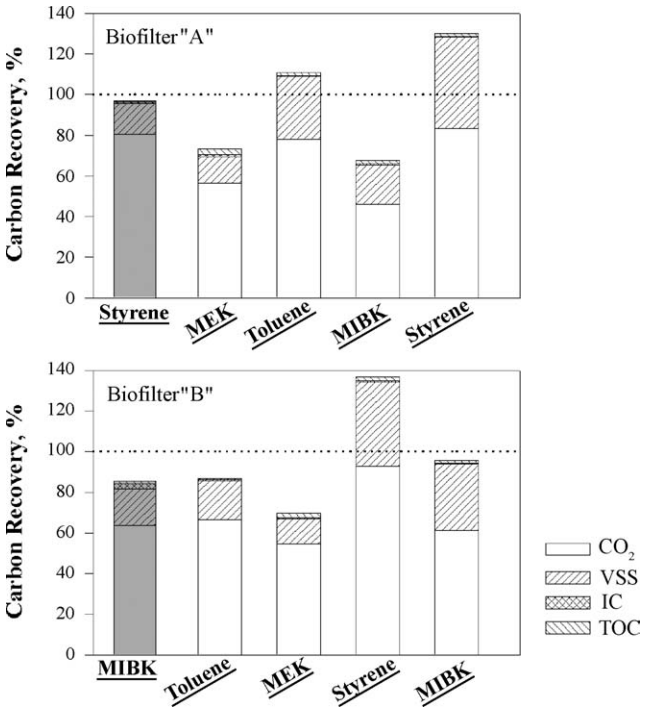

Fig. 6. Carbon recovery for each feed VOC. (Greyed bars are developed based on the previous studies [6,14]).

mated amount of biomass accumulated in each bed prior to toluene feeding was 34.4 and 74.16 g for biofilter "A" and biofilter "B", respectively. The greater biomass that was estimated to have been added in biofilter "B" may explain why it initially recovered to 99% removal efficiency more rapidly than biofilter "A" after the initial switch to feeding toluene. However, biofilter "B" later exhibited less stable behavior as toluene concentration was increased (see Fig. 3).

4. Conclusions and recommendations

The present study demonstrated the effect of interchanging the feed VOCs on the behavior of the biofilter. The specific conclusions and recommendations that can be drawn from this study include the following:

1. As observed in each biofilter, in which a single VOC was fed without an interchange of the feed VOCs, high removal efficiencies were also observed when interchanging VOCs.
2. The biofilter recovered quickly to the 99% – removal level after interchanging to MEK or MIBK (oxygenated compounds), regardless of the immediately preceding compound fed to each biofilter. However, after interchanging to toluene or styrene removal (aromatic compounds), a longer reacclimation period was required. The biofilter response after interchange of feed VOCs appeared to depend on the physicochemical property of feed VOCs as well as the biomass retained in the biofilter prior to interchanging the VOC.
3. The data obtained from this study support the hypothesis that when treating VOCs at their critical loading rate, biofilter performance may be improved by employing a lower EBRT if the loading rate is high (corresponding to higher inlet concentration), such as was the case for MEK in this study. The improvement may be a result of oxygen limitation within the biofilm at high concentrations and longer EBRT.
4. For the four compounds studied, a first order kinetics model was a good approximation to describe the substrate degradation except in the case of very high inlet concentration of MEK, where oxygen limitation may have been a factor.
5. Immediately after interchanging the feed VOCs, a smaller ratio of COD/N and a larger ratio of CO_2/COD were observed.
6. Additional studies of microbial communities dynamics when interchanging the VOCs needs to be conducted to determine if the increased CO_2 production is a result of die-off or depletion of stored energy, or whether the same community is "gearing-up" to use the new compound, i.e., production of proteins and enzymes.

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