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# A comparative study in treating two VOC mixtures in trickle bed air biofilters

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## Abstract

Two independent parallel trickling bed air biofilters (TBABs) (“A” and “B”) with two different typical VOC mixtures were investigated. Toluene, styrene, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) were the target VOCs in the mixtures. Biofilter “A” was fed equal molar ratio of the VOCs and biofilter “B” was fed a mixture based on EPA 2003 emission report. Backwashing and substrate starvation operation were conducted as biomass control. Biofilter “A” and “B” maintained 99% overall removal efficiency for influent concentration up to 500 and 300 ppmv under backwashing operating condition, respectively. The starvation study indicated that it can be an effective biomass control for influent concentrations up to 250 ppmv for biofilter “A” and 300 ppmv for “B”. Re-acclimation of biofilter performance was delayed with increase of influent concentration for both biofilters. Starvation operation helped the biofilter to recover at low concentrations and delayed re-acclimation at high concentrations. Furthermore, re-acclimation for biofilter “B” was delayed due to its high toluene content as compared to biofilter “A”. The pseudo first-order removal rate constant decreased with increase of volumetric loading rate for both biofilters. MEK and MIBK were completely removed in the upper 3/8 media depth. While biofilter depth utilization for the removal of styrene and toluene increased with increase of influent concentrations for both biofilters. However, toluene removal utilized more biofilter depth for biofilter “B” as compared to biofilter “A”.

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**Keywords:** Backwashing; Biodegradation; Biofiltration; Starvation; Trickle bed air biofilter; Volatile organic compounds (VOCs)

## 1. Introduction

Emission control of volatile organic compounds (VOCs) has become one major concern in air pollution prevention since the 1990 Clean Air Act Amendments went into effect. Biotreatment of VOCs offers an inexpensive alternative to conventional technologies (Don and Feenstra, 1984; Ottengraf, 1986). Biofiltration has emerged as a reliable and cost-effective technology for the control of VOCs emissions. Trickling-bed air biofilters (TBABs) facilitate more consistent operation than traditional biofilters due to better control of overall pressure drop, nutrient concentration,

and pH. During the past decade, many studies concerning the treatment of contaminated gas stream by biofiltration had been conducted (Sorial et al., 1994, 1995; Zhu et al., 1996; Arnold et al., 1997; Chou and Huang, 1997; Cox and Deshusses, 1998; Wu et al., 1999; Bibeau et al., 2000; Delhomenie et al., 2002; Cai et al., 2004, 2005). Most of the studies were involved in treating single VOC. However, many industrial air emissions contain mixtures of VOCs that possess various physical and chemical properties affecting their biological treatment.

Studies on removal of VOC mixtures by biofiltration are reported by a number of researchers (Deshusses et al., 1996; Mohseni and Allen, 1999, 2000; Yoon and Park, 2002; Aizpuru et al., 2003a,b; Chang and Lu, 2003; Atoche and Moe, 2004; Moe and Qi, 2004). Deshusses et al. (1996) investigated the transient-state behavior of a biofilter removing mixtures of methyl ethyl ketone (MEK) and

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methyl isobutyl ketone (MIBK) from air. Mohseni and Allen (1999, 2000) studied transient and long-term performance of methanol and  $\alpha$ -pinene mixture. They found that the biofilters had much higher removal capacity to methanol ( $170\text{--}180\text{ g m}^{-3}\text{ h}^{-1}$ ) than those to  $\alpha$ -pinene ( $45\text{ g m}^{-3}\text{ h}^{-1}$ ) with empty bed retention time (EBRT) as low as 20 s. Most of the methanol was removed in the top section of the biofilter, and  $\alpha$ -pinene degradation utilized the whole biofilter depth. Yoon and Park (2002) studied the effect of operation parameters on VOC mixtures removal performance in a peat-packed biofilter. They found there was an optimum operation temperature for VOC mixtures removal at  $32\text{ }^{\circ}\text{C}$  and lengthened EBRT could improve removal efficiency. Aizpuru et al. (2003a,b) investigated and compared 11 VOCs mixture performance in a peat biofilter and a biofilter packed with granular activated carbon. They found that the packing materials played an important role in the removal stratification of VOCs concerned. Chang and Lu (2003) investigated the performance of toluene and acetone mixture in a trickle-bed air biofilter. They found that the removal efficiency of toluene was higher than that of acetone.

Non-use operation occurs periodically in industry due to shut-off during weekends and holidays. In experiments where the influent contaminant loading was suspended for longer periods (2 d to 2 wk), diminished contaminant removal for a period lasting several hours or even few days following resumption of contaminant loading had been reported (Mohseni et al., 1998; Webster et al., 1999; Wani et al., 2000; Metris et al., 2001; Park and Kinney, 2001; Cox and Deshusses, 2002; Cai et al., 2004, 2005; Moe and Qi, 2004; Kim et al., 2005a,b). Cai et al. (2004, 2005) and Kim et al. (2005a,b) found that non-use periods did not have noticeable adverse effect on removal efficiency when the employed loading rates did not exceed the elimination capacity of the biofilters and non-use operation could be employed as a means of biomass control for these loading rates. Only one investigation of non-use operation for VOC mixtures was reported. Moe and Qi (2004) studied the performance of a fungal biofilter treating *n*-butyl acetone, MEK, methyl propyl ketone (MPK), and toluene mixtures during intermittent loading. They found that shutdown of loading had varying effects on removal efficiency for different compounds. Shutdown had no noticeable adverse affect on removal of *n*-butyl acetone while removal of MEK and MPK was impacted for a few hours, and toluene removal was adversely impacted for a few days.

The objective of this research was to evaluate the performance of TBAB for VOC mixtures (ketones and aromatic compounds) under different loading conditions. The goal was to maintain consistently high removal efficiencies for long-term operation and determine the critical loading capacity. The evaluations are focused on the following parameters: (1) mixture loading; (2) recovery of biofilter performance after backwashing and starvation operation; (3) nitrogen utilization; (4) development of

preliminary kinetic data; and (5)  $\text{CO}_2$  (carbon mass balance) closures.

## 2. Materials and methods

### 2.1. Mixtures of volatile organic compounds

The VOCs used were two oxygenated compounds, namely, MEK and MIBK and two aromatic compounds styrene and toluene (Fisher Scientific, Fair Lawn, NJ, pure 99%). These VOCs are common solvents employed in industry and are major components of paints and varnishes. The dimensionless Henry's law constants for toluene, styrene, MEK and MIBK are 0.280, 0.109, 0.00194, and 0.00062 (Verschuere, 2001), respectively. Two different VOC mixtures were employed in this study. The first one, fed to biofilter "A", was an equal molar ratio of the four VOCs. The second one, fed to biofilter "B", was a mixture based on EPA 2003 emission report from chemical industry. The molar ratio of the four VOCs on biofilter "B" was 0.448:0.260:0.234:0.058 for toluene:styrene:MEK:MIBK, respectively.

### 2.2. Trickle biofilter

The biofilter continued to be run without reconditioning the media used in pervious runs where the four VOCs were interchanged as the sole VOC contaminant (Cai et al., 2006). An illustration of the biofilter system is provided in a previous study (Cai et al., 2005). The biofilter was constructed of seven cylindrical glass sections with an internal diameter of 76 cm and a total length of 130 cm. The reactor was packed with pelletized diatomaceous earth as biological support media to a depth of about 60 cm (Celite 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA). The biofilter was run at constant operating temperature of  $20\text{ }^{\circ}\text{C}$  and operated in a co-current gas and liquid downward flow mode.

Air flow was set up at the rate of  $1.35\text{ l min}^{-1}$  with corresponding EBRT of 2.02 min. These conditions were chosen based on our previous study for styrene biodegradation, which required the highest EBRT for the four VOCs (Cai et al., 2004, 2005; Kim et al., 2005a,b). Liquid VOC was injected via a syringe pump and vaporized into the air stream. Each VOC inlet mixture concentration was stepwise increased from 50 ppmv to the maximum allowable inlet mixture concentration, for attaining over 99% removal. Buffered nutrient solution was supplied at a rate of  $2.4\text{ l d}^{-1}$ , the composition of the nutrient solution was provided in a previous study (Sorial et al., 1995). *In situ* upflow backwashing with media fluidization was employed at a rate of 1 h a week as a strategy for biomass control during the backwashing experimental periods. However no backwashing was employed during starvation experimental periods. During starvation (2 d/wk) only pure air and nutrients solution was allowed to pass through the

Table 1  
Biofilter operating conditions

| Experimental stage  | I    | II   | III  | IV   | V              |      |
|---|------|------|------|------|----------------|------|
| Concentration, ppmv   | 50   | 100  | 250  | 500  | 1000           |      |
| <i>Biofilter "A"</i>  |      |      |      |      |                |      |
| Toluene loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> )            | 0.11 | 0.22 | 0.54 | 1.07 | 2.14           |      |
| Styrene loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> )            | 0.12 | 0.24 | 0.60 | 1.19 | 2.39           |      |
| MEK loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> )                | 0.07 | 0.13 | 0.33 | 0.66 | 1.32           |      |
| MIBK loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> )               | 0.10 | 0.20 | 0.51 | 1.02 | 2.03           |      |
| Total loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> ) <sup>a</sup> | 0.40 | 0.79 | 1.98 | 3.94 | 7.88           |      |
| Experimental stage  | I    | II   | III  | IV   | V <sup>b</sup> | VI   |
| Concentration (ppmv)  | 50   | 100  | 250  | 500  | 350            | 300  |
| <i>Biofilter "B"</i>  |      |      |      |      |                |      |
| Toluene loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> )            | 0.19 | 0.38 | 0.96 | 1.92 | 1.34           | 1.15 |
| Styrene loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> )            | 0.12 | 0.25 | 0.62 | 1.24 | 0.87           | 0.74 |
| MEK loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> )                | 0.06 | 0.12 | 0.31 | 0.62 | 0.43           | 0.37 |
| MIBK loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> )               | 0.02 | 0.05 | 0.12 | 0.24 | 0.17           | 0.14 |
| Total loading rate (kg COD m <sup>-3</sup> d <sup>-1</sup> ) <sup>a</sup> | 0.39 | 0.80 | 2.01 | 4.02 | 2.81           | 2.40 |

<sup>a</sup> Loading conversion factor the VOC mixtures: biofilter "A": 1 kg COD m<sup>-3</sup> d<sup>-1</sup> = 14.55 g m<sup>-3</sup> h<sup>-1</sup>; biofilter "B": 1 kg COD m<sup>-3</sup> d<sup>-1</sup> = 14.15 g m<sup>-3</sup> h<sup>-1</sup>.

<sup>b</sup> Stage V: biofilter B was conducted with backwashing operation only.

biofilter. The conditions employed during the experimental runs are summarized in Table 1.

### 2.3. Analytical methods

The concentrations of VOCs in the gas phase were measured by using a gas chromatograph (GC) (HP 5890, Series II, Hewlett–Packard, Palo Alto, CA) equipped with a flame ionization detector (FID). A GC (HP 5890, Series II, Hewlett–Packard, Palo Alto, CA) equipped with a thermal conductivity detector (TCD) was used for determining the CO<sub>2</sub> concentrations in the effluent gas phase. A detailed method for GC–FID and GC–TCD is provided in a previous publication (Cai et al., 2005). Liquid phase samples were analyzed for NO<sub>3</sub><sup>-</sup>, total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. NO<sub>3</sub><sup>-</sup> was determined according to Standard Methods 4500-NO<sub>3</sub><sup>-</sup> B (APHA, AWWA, WPCF, 1998) by using a Shimadzu UVmini 1240 UV–Vis spectrophotometer (Shimadzu Corp., Tokyo, Japan). TC and IC were determined by using a Shimadzu TOC 5050 analyzer (Shimadzu Corp., Tokyo, Japan) according to Standard Methods 5310 (APHA, AWWA, WPCF, 1998). The VSS concentrations in the effluent and backwashing water were determined according to Standard Methods 2540 G (APHA, AWWA, WPCF, 1998).

## 3. Results and discussion

### 3.1. Biofilter performance

Biofilter "A" and "B" were both started up at 50 ppmv inlet mixture concentration with 2.02 min EBRT, and 17.1 mmol NO<sub>3</sub><sup>-</sup>-N d<sup>-1</sup>. The operating conditions are summarized in Table 1.

Biofilter "A" got re-acclimated and maintained 99% overall removal efficiency for inlet mixture concentrations

up to 500 ppmv with a total corresponding loading rate of 3.94 kg COD m<sup>-3</sup> d<sup>-1</sup> under backwashing operation with toluene removal efficiency round 95%. When the total concentration was increased further to 1000 ppmv with a corresponding loading rate of 7.88 kg COD m<sup>-3</sup> d<sup>-1</sup>, the biofilter performance did not get re-acclimated to the original performance and the overall removal efficiency could just be maintained at around 80%. With regards to the mixture components, toluene removal efficiency decreased sharply to round 50% and styrene removal efficiency decreased to around 82%. However, the removal efficiencies for MEK and MIBK were maintained over 99% for all employed influent concentrations. Biofilter "A" performance under starvation operation decreased to 95% and 70% when the inlet mixture concentration was increased to 500 and 1000 ppmv, respectively. The performance under starvation operation indicated that it had adverse effect on the biofilter performance when the employed loading exceeded 3.94 kg COD m<sup>-3</sup> d<sup>-1</sup>.

Biofilter "B" showed significant different performance as compared to biofilter "A". The biofilter maintained 99% removal efficiency for loading rates up to 2.41 kg COD m<sup>-3</sup> d<sup>-1</sup> (300 ppmv inlet mixture concentration) for both operations (backwashing and starvation). However, the overall removal efficiency decreased to 95% and further to 90% when the inlet mixture concentration increased to 350 and 500 ppmv, respectively, for backwashing strategy. The performance under starvation operation decreased to 80% for inlet mixture concentration 500 ppmv. The removal efficiencies of styrene, MEK, and MIBK in biofilter "B" were maintained at 99% for all employed loading rates for the backwashing strategy. For starvation strategy, styrene took longer time to get re-acclimated to attain the 99% removal level for an inlet mixture concentration of 500 ppmv. However, the removal efficiency for toluene decreased to 85% and 60–80% for backwashing and starva-



tion strategies, respectively, when the inlet mixture concentration increased to 500 ppmv.

The elimination capacity for biofilter “A” with respect to loading rate is presented in Fig. 1. Fig. 1a indicates that under the backwashing strategy, the biofilter elimination capacity for the mixture is similar to toluene elimination capacity in a single solute study (Kim et al., 2005a). The critical loading for the mixture at which over 99% overall efficiency is attained was  $3.94 \text{ kg COD m}^{-3} \text{ d}^{-1}$ . However, the toluene critical loading in biofilter “A” was  $1.03 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $13.73 \text{ g m}^{-3} \text{ h}^{-1}$ ), which was much lower than that in the single solute study ( $3.52 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $46.92 \text{ g m}^{-3} \text{ h}^{-1}$ )). Meanwhile, styrene critical loading in biofilter “A” under the backwashing strategy was  $1.87 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $25.36 \text{ g m}^{-3} \text{ h}^{-1}$ ), which was similar to the single solute study ( $1.90 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $25.77 \text{ g m}^{-3} \text{ h}^{-1}$ )) (Kim et al., 2005b). Therefore, it can be deduced that the elimination capacity of styrene, MEK, and MIBK under backwashing strategy in biofilter “A” was not significantly affected by the presence of the other VOCs, however, the removal of toluene was significantly affected. On the other hand, the biofilter elimination capacity decreased under starvation strategy when the loading rate exceeded  $3.94 \text{ kg COD m}^{-3} \text{ d}^{-1}$  as shown in Fig. 1b. The critical loadings for toluene and styrene in bio-

filter “A” under starvation strategy were at  $0.94$  and  $1.20 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $12.53$  and  $16.27 \text{ g m}^{-3} \text{ h}^{-1}$ ), respectively. No critical loading for MEK and MIBK in the biofilter could be determined for both backwashing and starvation strategies because at all concentration levels studied the removal for both components were above 99%.

The elimination capacity for biofilter “B” was much lower than that for biofilter “A” (data not shown). The critical mixture loading for biofilter “B” was  $2.40 \text{ kg COD m}^{-3} \text{ d}^{-1}$ . The toluene critical loading under backwashing strategy was  $1.30 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $17.33 \text{ g m}^{-3} \text{ h}^{-1}$ ). No critical loading for styrene, MEK and MIBK could be determined because at all mixture concentration levels studied the removal was above 99%. Under starvation strategy, the toluene critical loading was  $1.13 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $15.06 \text{ g m}^{-3} \text{ h}^{-1}$ ) and the styrene critical loading was  $1.20 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $16.27 \text{ g m}^{-3} \text{ h}^{-1}$ ).

The overall employed loading rates were similar for both biofilters under the same overall influent concentrations (see Table 1). The major difference between the two biofilters was toluene and MIBK contents. It is worthwhile to note that there is no significant difference in performance between the two biofilters with respect to styrene, MEK, and MIBK. However, the overall performance of biofilter “B” was poor as compared to biofilter “A” which could be attributed to the higher toluene content in biofilter “B”.

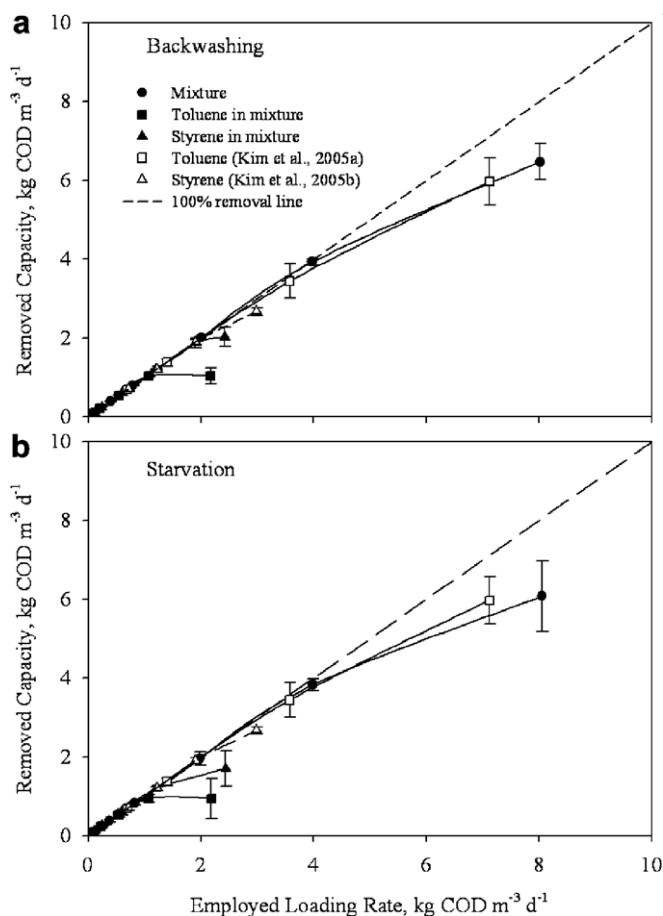


Fig. 1. Biofilter “A” elimination capacity with respect to loading rate.

### 3.2. Biofilter response after backwashing and starvation operation

Effluent samples were collected at prescheduled time intervals to evaluate biofilter response after backwashing and starvation. Re-acclimation was considered to have been achieved when 99% of the original performance was attained. Tables 2 and 3 indicate that the recovery of biofilter performance was delayed with increase of loading rate for both mixtures. Under backwashing strategy, both biofilters recovered to 99% removal efficiency for an overall influent concentration up to 500 ppmv (biofilter “A”) and 300 ppmv (biofilter “B”). However, under starvation strategy, the biofilters could just recover to 99% level at an overall influent concentration up to 250 and 300 ppmv for biofilter “A” and biofilter “B”, respectively.

The starvation strategy helped the biofilter recover its original performance at lower inlet mixture concentration due to more available biomass without causing adverse effect. However, at high inlet mixture concentration, starvation operation decreased the overall performance of the biofilters due to excess biomass retained in the biofilters. Furthermore, it is noticed that each biofilter obtained a higher removal level just after re-starting from starvation operation. The initial higher removal level could be attributed to the adsorption of VOCs by the accumulated biomass in the biofilter and not due to biodegradation because of the decreased performance after the initial high removal level and then recovering gradually to a high level

Table 2  
Biofilter “A” response after backwashing and starvation

| Removal efficiency (%) |     |     |     |     |     |     |     |      |      |
|------------------------|-----|-----|-----|-----|-----|-----|-----|------|------|
| Time (min)             | 30  | 60  | 90  | 120 | 180 | 300 | 360 | 1200 | 2880 |
| <i>Backwashing</i>     |     |     |     |     |     |     |     |      |      |
| Time (min)             | 30  | 60  | 90  | 120 | 180 | 300 | 360 | 1200 | 2880 |
| 50 ppmv                | 87  | 95  | 98  | 99  | 100 | 100 | 100 | 100  | 100  |
| 100 ppmv               | 85  | 89  | 89  | 93  | 97  | 100 | 100 | 100  | 100  |
| 250 ppmv               | 89  | 87  | 83  | 88  | 96  | 100 | 100 | 100  | 100  |
| 500 ppmv               | 81  | 84  | 79  | 82  | 93  | 99  | 100 | 100  | 100  |
| 1000 ppmv              | 79  | 80  | 73  | 73  | 79  | 81  | 81  | 82   | 81   |
| <i>Starvation</i>      |     |     |     |     |     |     |     |      |      |
| Time, min              | 30  | 60  | 90  | 120 | 180 | 300 | 360 | 1200 | 2880 |
| 50 ppmv                | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100  | 100  |
| 100 ppmv               | 99  | 93  | 96  | 99  | 100 | 100 | 100 | 100  | 100  |
| 250 ppmv               | 96  | 93  | 99  | 97  | 100 | 100 | 100 | 100  | 100  |
| 500 ppmv               | 99  | 96  | 94  | 88  | 90  | 93  | 92  | 95   | 95   |
| 1000 ppmv              | 93  | 94  | 95  | 79  | 65  | 83  | 74  | 70   | 71   |

Table 3  
Biofilter “B” response after backwashing and starvation

| Removal efficiency (%) |    |    |    |     |     |     |     |      |      |
|------------------------|----|----|----|-----|-----|-----|-----|------|------|
| Time (min)             | 30 | 60 | 90 | 120 | 180 | 300 | 360 | 1200 | 2880 |
| <i>Backwashing</i>     |    |    |    |     |     |     |     |      |      |
| 50 ppmv                | 83 | 94 | 94 | 96  | 96  | 98  | 100 | 100  | 100  |
| 100 ppmv               | 78 | 88 | 88 | 90  | 93  | 95  | 100 | 100  | 100  |
| 250 ppmv               | 76 | 82 | 85 | 87  | 88  | 93  | 99  | 100  | 100  |
| 300 ppmv               | 75 | 80 | 82 | 86  | 88  | 92  | 95  | 100  | 100  |
| 350 ppmv               | 72 | 69 | 81 | 84  | 86  | 89  | 94  | 95   | 96   |
| 500 ppmv               | 71 | 75 | 79 | 81  | 83  | 87  | 90  | 88   | 91   |
| <i>Starvation</i>      |    |    |    |     |     |     |     |      |      |
| 50 ppmv                | 83 | 62 | 76 | 100 | 100 | 100 | 100 | 100  | 100  |
| 100 ppmv               | 87 | 83 | 70 | 82  | 100 | 100 | 100 | 100  | 100  |
| 250 ppmv               | 98 | 89 | 73 | 64  | 85  | 91  | 100 | 100  | 100  |
| 300 ppmv               | 98 | 87 | 77 | 68  | 83  | 99  | 100 | 100  | 100  |
| 500 ppmv               | 94 | 91 | 83 | 63  | 77  | 80  | 83  | 80   | 82   |

performance. Meanwhile, re-acclimation required longer time for biofilter “B” due to the higher toluene content in the mixture as compared to biofilter “A”. The re-acclimation of each component in the mixtures (data not shown) indicated that the required re-acclimation period was controlled by the re-acclimation of toluene and styrene in the mixtures. Re-acclimation of MEK and MIBK for both mixtures was within 30 min for all loading rates studied.

### 3.3. Nitrogen utilization and VOCs removal

Daily analyses for the influent and effluent concentrations of  $\text{NO}_3^-$ -N were conducted. The net nitrogen utilization was calculated by subtracting the amount of the  $\text{NO}_3^-$  species in the effluent water from the  $\text{NO}_3^-$  species present in the nutrient feed. COD removal was calculated as the difference between the COD of the feed and the COD of the effluent gas and liquid streams. Fig. 2 shows COD/N ratios plotted against the sequential date for biofilter “A”.

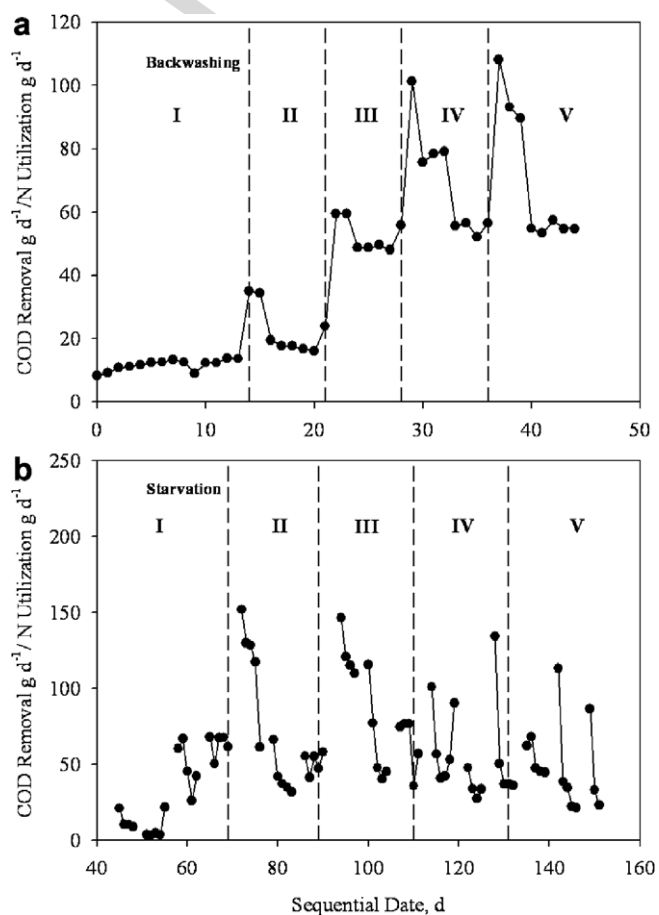


Fig. 2. COD removal per nitrogen utilization under backwashing and starvation for biofilter “A”.

The ratios in Fig. 2a under backwashing strategy show apparent dependency on the employed loading rate and time. As the employed loading rate was increased up to  $1.98 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $28.67 \text{ g m}^{-3} \text{ h}^{-1}$ ) (stage III), the ratio of COD/N increased. When the loading rate exceeded  $1.98 \text{ kg COD m}^{-3} \text{ d}^{-1}$ , the ratios of COD/N remained con-

stant at around 55 g COD/g N after the initial acclimation of the biofilter. The decrease of nitrogen utilization with increase of loading rate up to  $1.98 \text{ kg COD m}^{-3} \text{ d}^{-1}$  ( $28.67 \text{ g m}^{-3} \text{ h}^{-1}$ ) could be due to a decrease in microbial viability. When the loading rate was further increased, stability in microbial viability is reached after initial acclimation of the biofilter to the new loading rate. Furthermore, it is noticed that as the loading rate was increased, longer time was required to attain stable COD/N ratio which is consistent with the VOC removal described previously.

However, the ratios of COD/N in Fig. 2b for starvation strategy did not show apparent dependency on loading, which could mean that the microbial viability reached stability under starvation operation due to retained biomass in the biofilter. Meanwhile it showed dependency on time in each starvation cycle. The ratios of COD/N were high just after re-start from starvation period and then decreased quickly to a relative stable value (around 45 g COD/g N). The transition period in ratios of COD/N from high to stable values for each starvation cycle could be attributed to the process regaining stable microbial viability after re-start from starvation period.

The nitrogen utilization for biofilter “B” (data not shown) was similar to biofilter “A” and the ratios of COD/N after stabilization were 40 and 45 g COD/g N for backwashing and starvation operation, respectively.

### 3.4. Kinetics analysis of biofilter performance

One day following backwashing, gaseous samples were taken along the media depth of the biofilter to assess the removal kinetics for both mixtures. The kinetic analyses were based on pseudo first-order removal rate as a function of biofilter depth. By plotting the natural logarithmic scale of the ratio of residual concentration of each component in the mixture to its inlet concentration as a function of depth into the biofilter (expressed as the cumulative EBRT), i.e., ( $\ln(C/C_0)$  vs. time), the pseudo first order removal rate constants were obtained from the slopes of the regression lines.

Fig. 3 represents plots of the first order removal rate constants of toluene and styrene in the two biofilters under the different loading rates for the two operating conditions considered in this study. No rate constants could be obtained for MEK and MIBK because they were removed completely in the upper 3/8 biofilter media bed at all employed concentrations in this study.

The result in Fig. 3 indicates that the removal rate constants decreased as the employed loading rates increased for toluene and styrene in both biofilters. The effect of starvation operation showed apparent transition from positive to negative for both biofilters, which is consistent with the biofilter performance. The corresponding constants for biofilter “A” are apparently greater than those for biofilter “B” for toluene and styrene under similar loading rates. Lower constant values for toluene in biofilter “B” could be contributed to the much higher toluene content in the

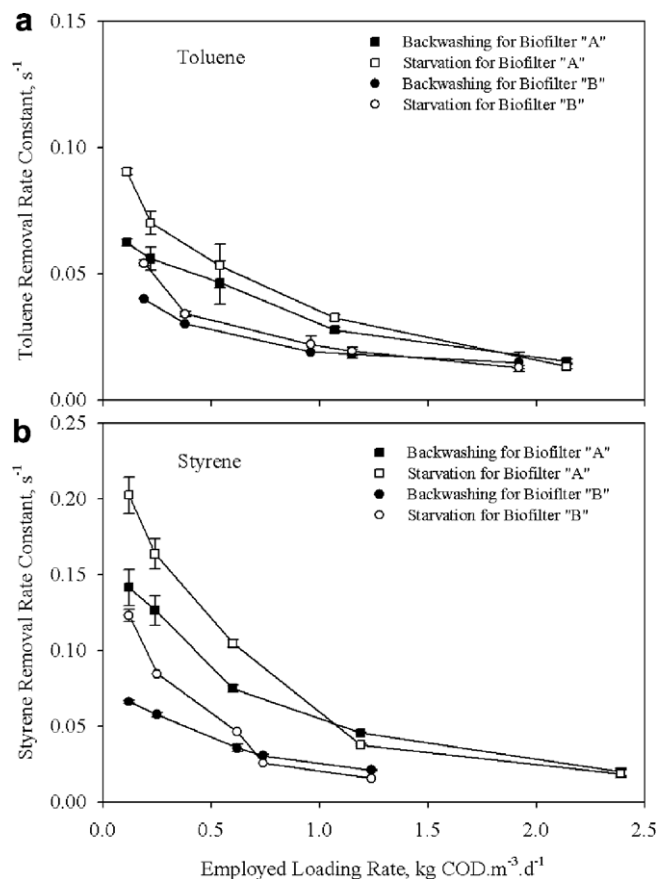


Fig. 3. COD removal per nitrogen utilization under backwashing and starvation for biofilter “A”.

mixture than that in biofilter “A” (see Table 1). The different constants for styrene in the two biofilters could indicate that styrene is affected by the relative concentration of the other components in the mixtures. Since the overall performances of the two biofilters with respect to styrene were similar, hence the difference in removal rates indicates more utilization of biofilter depth for biofilter “A” as compared to “B”.

On comparing rate constants from our previous single solute study (Kim et al., 2005a,b) to the current mixture study, it can be seen that toluene was significantly impacted by the presence of other components (see Fig. 3a). However, styrene removal rate constants in Fig. 3b showed slight difference between the single solute and the two mixtures studied. This behavior could indicate that toluene biodegradation along the biofilter depth was affected significantly by the other VOCs in the mixtures and styrene biodegradation was not affected.

### 3.5. CO<sub>2</sub> closure (carbon mass balance)

The cumulative CO<sub>2</sub> equivalent of VOCs consumed in the mixtures during all experimental runs was compared to the cumulative CO<sub>2</sub> produced within the biofilter (Fig. 4). The inlet (or outlet) cumulative CO<sub>2</sub> was estimated

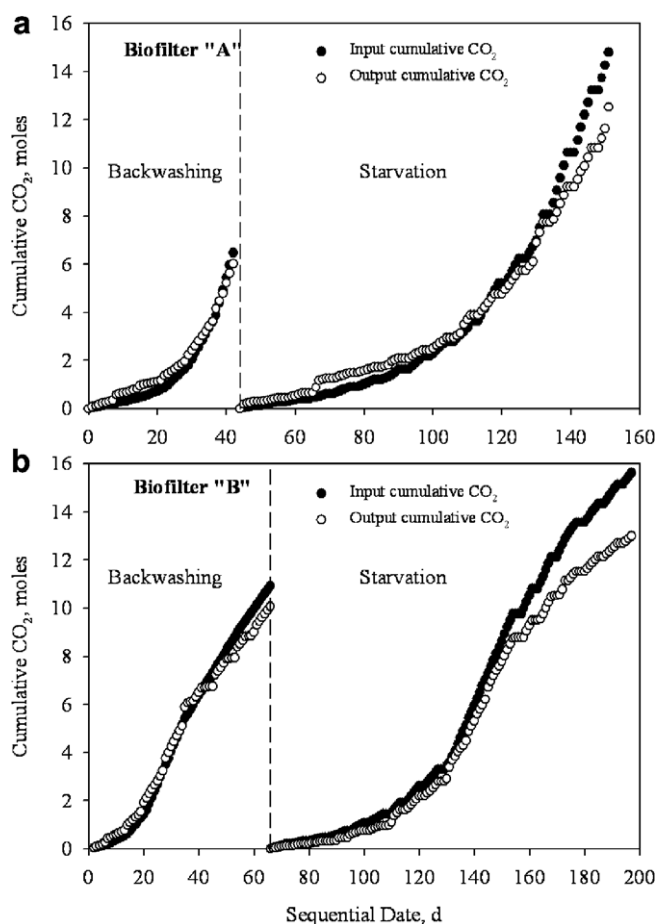


Fig. 4. Development of carbon balance with time ( $\text{CO}_2$  closure).

as the total cumulative  $\text{CO}_2$  in the influent (or effluent) aqueous and gaseous stream. For biofilter "A", the outlet cumulative  $\text{CO}_2$  was about 98% and 85% of the inlet cumulative  $\text{CO}_2$  for backwashing and starvation operation, respectively. For biofilter "B", the outlet cumulative  $\text{CO}_2$  was about 97% and 83% of the inlet cumulative  $\text{CO}_2$  for backwashing and starvation operation, respectively. The results indicate that the cumulative  $\text{CO}_2$  provided a very good closure for backwashing operation for both mixtures. The large deviations between the input cumulative  $\text{CO}_2$  and the output cumulative  $\text{CO}_2$  for starvation operation could be due to unwashed biomass within the biofilter which is not accounted for and might also be due to indigenous respiration during starvation periods which were not also accounted.

#### 4. Conclusions

This study investigated biofilter performance on two parallel trickling biofilters for two VOC mixtures. Step change in VOC concentrations revealed that over 99% removal efficiency could be maintained at an inlet mixture concentrations up to 500 ppmv (loading rate  $3.94 \text{ kg COD m}^{-3} \text{ d}^{-1}$ ) and 300 ppmv (loading rate  $2.40 \text{ kg COD m}^{-3} \text{ d}^{-1}$ ) for biofilter "A" and biofilter "B", respectively. Toluene content in

the mixtures played a major role in the biofilter overall performance. Furthermore, starvation operation helped in maintaining high level performance and could be used as another means of biomass control provided the inlet mixture concentration did not exceed 250 ppmv ( $2.01 \text{ kg COD m}^{-3} \text{ d}^{-1}$ ) and 300 ppmv ( $2.40 \text{ kg COD m}^{-3} \text{ d}^{-1}$ ) for biofilter "A" and biofilter "B", respectively.

Biofilter re-acclimation study shows that re-acclimation was delayed for both biofilters with increase of inlet mixture concentrations. The performance of biofilter "B" required longer time to recover than that of biofilter "A" due to the higher toluene content in biofilter "B".

Nitrogen utilization investigation indicates that biofilters required a transition period to get re-acclimated to new operating conditions and nitrogen utilization showed corresponding changing. There is no apparent difference in nitrogen utilization for the two biofilters.

VOCs removal kinetic analysis indicates that biofilter depth utilization increased with increase of inlet mixture concentrations for both biofilters. MEK and MIBK in the mixtures were removed in the upper biofilter depth, and removal of styrene and toluene utilized more biofilter depth. Meanwhile, biofilter "B" had higher removal rates for toluene and styrene than biofilter "A". The removal rate constant for toluene in the two mixtures studied were significantly different from the single solute.

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