

Biological Oxidation of Gaseous VOC Mixtures in a Trickle-Bed Air Biofilter

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Abstract: Two VOC mixtures with different compositions were fed to a Trickle-bed air biofilter with step-change in influent mixture concentrations from 50 ppmv to 1000 ppmv. The empty bed retention time was maintained at 2.02 min. Backwashing was conducted once a week as biomass control. The biofilter maintained 99% overall removal efficiency after start-up when the influent concentration did not exceed 500 ppmv (3.94 kg COD/m³-day) and 300 ppmv (2.41 kg COD/m³-day) for mixture 1 and mixture 2, respectively. Re-acclimation of the biofilter performance was delayed with increase of influent concentration for both mixtures. The re-acclimation for mixture 2 as compared to mixture 1 was delayed due to its higher toluene content. Removal behaviors of MEK, MIBK, and styrene along the biofilter depth were similar for both mixtures. However, toluene removal utilized more biofilter depth for mixture 2 as compared to mixture 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 (CAAA) went into effect. Biotreatment of VOCs offers an inexpensive alternative to conventional technologies such as catalytic and thermal oxidations, wet scrubbing, ozonation, and activated carbon adsorption (1, 2). 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 do via 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 (3-9). Most of the studies were involved in treating single VOC, and factors found to affect the decontamination efficiency include: nature of the contaminants, packing materials and configurations, empty bed retention time (EBRT), volumetric loading rates, nutrient feed flow rates, nutrient solution pH, and flow patterns of air. However, many industrial air emissions contain mixtures of VOCs that possess various physical and chemical properties affecting their biological treatment.

Studies on mixtures of VOCs for biofiltration are relatively scarce (10-14). Aizpuru et al. (10) investigated and compared 11 VOCs mixture performance in a peat biofilter and a biofilter packed with granular activated carbon (GAC). They found that the packing materials played an important role in

the removal stratification of VOCs. For the peat biofilter, elimination of oxygenated compounds occurred in the first 50 cm of the column. In contrast, for packing materials of GAC, the removal of oxygenated and aromatic compounds took place along the whole column. Meanwhile, two types of biofilters did not provide successful removal for chlorinated compounds although the peat biofilter had higher removal of the chlorinated compounds (60%) than the GAC biofilter (20%). Chang and Lu (11) 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. Moe and Qi (12) studied the performance of a fungal biofilter treating n-butyl acetone, methyl ethyl ketone (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 effect 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. Furthermore, the fungal biofilter required a longer time to recover for long term loading shutdown than shorter term shutdown. Mohseni et al. (13) studied transient and long-term performance of methanol and α -pinene mixture. They found that the biofilters had much higher removal capacity to methanol (170-180 g/m³/h) than those to α -pinene (45 g/m³/h) with empty bed retention time (EBRT) as low as 20 seconds. Most of methanol was removed in the top section of the biofilter, and α -pinene degradation utilized the whole biofilter depth. The α -

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pinene removal decreased in the top section with the increase of methanol inlet concentration. However, they found that methanol removal was not affected by the α -pinene step increase. Yoon and Park (14) 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 removal at 32 °C and a lengthened EBRT could improve the removal efficiency.

The objective of this research was to investigate the performance of TBAB for VOC mixtures. The goal was to maintain consistently high removal efficiencies for long-term operation. The evaluations are focused on the following operational parameters: (1) mixture loading, (2) recovery of biofilter performance after backwashing, (3) removal efficiency with biofilter depth under steady-state conditions.

Experimental Materials and Methods

The experimental work was performed on two independent parallel lab-scale TBABs for two different VOC mixtures. Two aromatic compounds (toluene and styrene) and two oxygenated compounds (methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK)) were employed in this study. The first mixture, namely mixture 1, was an equimolar ratio of toluene, styrene, MEK, and MIBK. The second mixture, namely mixture 2, was a typical ratio based on point source air emission in *EPA 2003 toxic release report* for chemical industries with a molar ratio of 0.448: 0.260: 0.234: 0.058 for toluene: styrene: MEK: MIBK, respectively.

The two TBABs, were named, "Mixture 1", and "Mixture 2" biofilters. Each TBAB was constructed of seven cylindrical glass sections with an internal diameter of 76 cm and a total length of 130 cm. The reactors were packed with pelletized diatomaceous earth biological support media to a depth of about 60 cm. The experimental runs were conducted at constant operating temperature of 20 °C. The TBABs were operated in a co-current gas and liquid downward flow mode.

The air flow was set up at the rate of 1.35 L/min for both TBABs with a corresponding empty bed retention time (EBRT) of 2.02 min. These conditions were chosen based on our previous studies for styrene biodegradation, which required the longest EBRT (8, 9, 15, 16). Liquid VOC mixtures were injected via a syringe pump and vaporized into the air stream. Inlet concentration was stepwise increased from 50 ppmv to 1000 ppmv and 500 ppmv for mixture 1 and 2, respectively. Buffered nutrient solution was supplied at a rate of 2.4 L/day for both biofilters.

In-situ upflow backwash was employed at a rate of 1 hour a week as a strategy for biomass control. The operating conditions for this experiment are summarized in Table 1 and 2.

Gas phase samples for VOC analysis were taken with gas-tight syringe and were measured by using a gas chromatograph (GC) equipped with a flame ionization detector (FID). A GC equipped with a thermal conductivity detector was used for determining the CO₂ concentration in the effluent gas. Liquid phase samples were analyzed for nitrate and volatile suspended solid (VSS) concentration, total carbon, and inorganic carbon.

Results and Discussion

Overview of Performance

The performance of the two biofilters with respect to VOCs removal is shown in Figures 1 and 2. The feed VOCs were introduced in the sequence shown in Tables 1 and 2 with respect to each biofilter. Re-acclimation was considered to have been achieved when 99% of the original biofilter performance was attained.

The results in Figure 1 show that "Mixture 1" biofilter became re-acclimated and maintained 99% overall removal efficiency for inlet concentrations up to 500 ppmv with a total corresponding loading rate of 3.94 kg COD/m³.day. But when the total concentration increased further to 1000 ppmv with a corresponding loading rate of 7.88 kg COD/m³.day, the biofilter performance did not become re-acclimated and the overall removal efficiency could just be maintained at around 80%. The removal efficiency for each component in the mixture is given in lower plots of Figures 1 and 2. From Figure 1 it is noticed that when the total influent concentration was increased to 500 ppmv, toluene removal efficiency decreased to round 95% although the overall removal efficiency was maintained above 99%. When the influent concentration was further increased to 1000 ppmv, toluene removal efficiency decreased sharply to approximately 50% although the overall removal efficiency was maintained around 80%. Meanwhile, styrene removal efficiency decreased to around 82% when the total influent concentration was increased to 1000 ppmv. However, the removal efficiencies for MEK and MIBK were maintained at 99% for all employed influent concentrations. On comparing each component loading rates at the 1000 ppmv inlet concentration (see Table 1) with the single solute critical loading rates for these four VOCs (3.52, 1.90, 5.63, and 3.26 kg COD/m³.day for toluene, styrene, MEK, and MIBK, respectively) obtained in

Table 1. “Mixture 1” Biofilter Operating Conditions

Experimental Stage	I	II	III	IV	V
	Sequential days				
Operational Periods in days	1-14	15-21	22-28	29-36	37-42
Overall Inlet concentration, ppmv	50	100	250	500	1000
Toluene loading rate, kg COD/m ³ .day	0.11	0.22	0.54	1.07	2.14
Styrene loading rate, kg COD/m ³ .day	0.12	0.24	0.60	1.19	2.39
MEK loading rate, kg COD/m ³ .day	0.07	0.13	0.33	0.66	1.32
MIBK loading rate, kg COD/m ³ .day	0.10	0.20	0.51	1.02	2.03
Total Loading rate, kg COD/m ³ .day	0.39	0.79	1.97	3.94	7.88
EBRT, min	2.02	2.02	2.02	2.02	2.02

Table 2. “Mixture 2” Biofilter Operating Conditions

Experimental Stage	I	II	III	IV	V	VI
	Sequential days					
Operational Periods in days	1-6	7-13	14-19	20-33	34-52	53-60
Overall Inlet concentration, ppmv	50	100	250	500	350	300
Toluene loading rate, kg COD/m ³ .day	0.19	0.38	0.96	1.92	1.34	1.15
Styrene loading rate, kg COD/m ³ .day	0.12	0.25	0.62	1.24	0.87	0.74
MEK loading rate, kg COD/m ³ .day	0.06	0.12	0.31	0.62	0.43	0.37
MIBK loading rate, kg COD/m ³ .day	0.02	0.05	0.12	0.24	0.17	0.14
Total Loading rate, kg COD/m ³ .day	0.40	0.80	2.01	4.02	2.81	2.41
EBRT, min	2.02	2.02	2.02	2.02	2.02	2.02

our previous studies (8, 9, 15, 16), the loading rates for toluene, MEK, and MIBK did not exceed the critical loading rates obtained from the single solute studies, but the loading rate for styrene exceeded its critical loading rate (1.90 kg COD/m³.day). Therefore, it can be deduced that the removal of styrene, MEK, and MIBK in the mixture was not affected by the presence of the other VOCs. On the other hand, the removal of toluene was significantly affected.

“Mixture 2” biofilter showed significant different performance from “Mixture 1” biofilter. The biofilter maintained 99% removal efficiency for loading rates up to 2.41 kg COD/m³.day (300 ppmv inlet concentration). However, the overall removal efficiency decreased to 95% when the influent concentration increased to 350 ppmv, and it decreased further to 90% when the influent concentration increased further to 500 ppmv. The removal efficiencies of styrene, MEK, and MIBK in “Mixture 2” biofilter was maintained at 99% for all employed loading rates in the studies. However, the removal efficiency for toluene decreased to 90% when the overall influent concentration increased to 350 ppmv. The highest loading rates in mixture 2 for all four VOCs (see Table 2) did not exceed their corresponding critical

loading rates in the single solute studies reported previously in our discussion for “Mixture 1” biofilter. Although the overall employed loading rates were similar for both mixtures under the same overall influent concentrations, “Mixture 2” biofilter performance was worse than “Mixture 1” biofilter. The major difference between mixture 1 and 2 was the toluene and MIBK contents in the mixtures. 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 “Mixture 2” biofilter was poor as compared to “Mixture 1” biofilter which could be contributed to the higher toluene content in “Mixture 2” biofilter.

Biofilter Re-acclimation after Backwashing

Effluent samples were collected at prescheduled time intervals to evaluate the biofilter response after backwashing. Table 3 shows the biofilter recovery following backwashing. Re-acclimation was considered to have been achieved when 99% of the original performance was attained. Table 3 indicates that the recovery of biofilter performance was delayed with increase of loading rate for both mixtures.

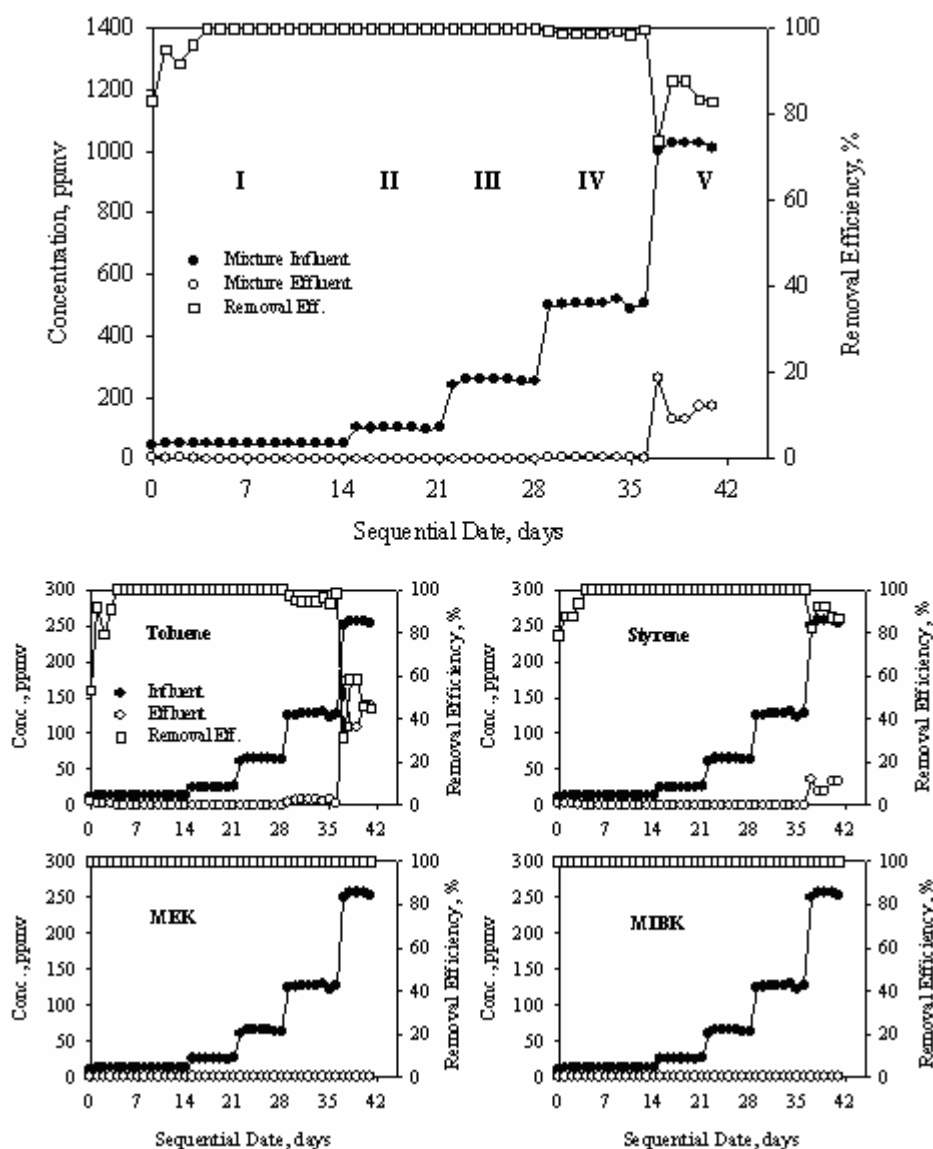


Figure 1. Performance of “Mixture 1” biofilter.

Biofilter performance could recover to 99% removal efficiency for “Mixture 1” and “Mixture 2” at an overall influent concentration up to 500 ppmv and 300 ppmv, respectively. Meanwhile, re-acclimation required longer time for “Mixture 2” biofilter due to higher toluene content in the mixture as compared to “Mixture 1” biofilter. The re-acclimation of each VOC in the mixture (data not shown) indicated that the required re-acclimation period was controlled by the re-acclimation of toluene and styrene in the mixture. Re-acclimation of MEK and MIBK for both mixtures was within 30 minutes for all loading rates studied.

The response time for the recovery of the four VOC components in the mixture for both biofilters clearly indicates the difference in the metabolism of

aromatic and oxygenated compounds. 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 (17).

Removal Profile along Biofilter Depth

One day following backwashing, gaseous samples were taken along the media depth of the biofilter to assess the removal along depth and depth utilization for both biofilters. Figure 3 represents plots of removal profile along biofilter depth for both biofilters. Figure 3 shows that the utilization of biofilter depth increased with the increase of VOC loading rate for both biofilters. Meanwhile, the removal profile of

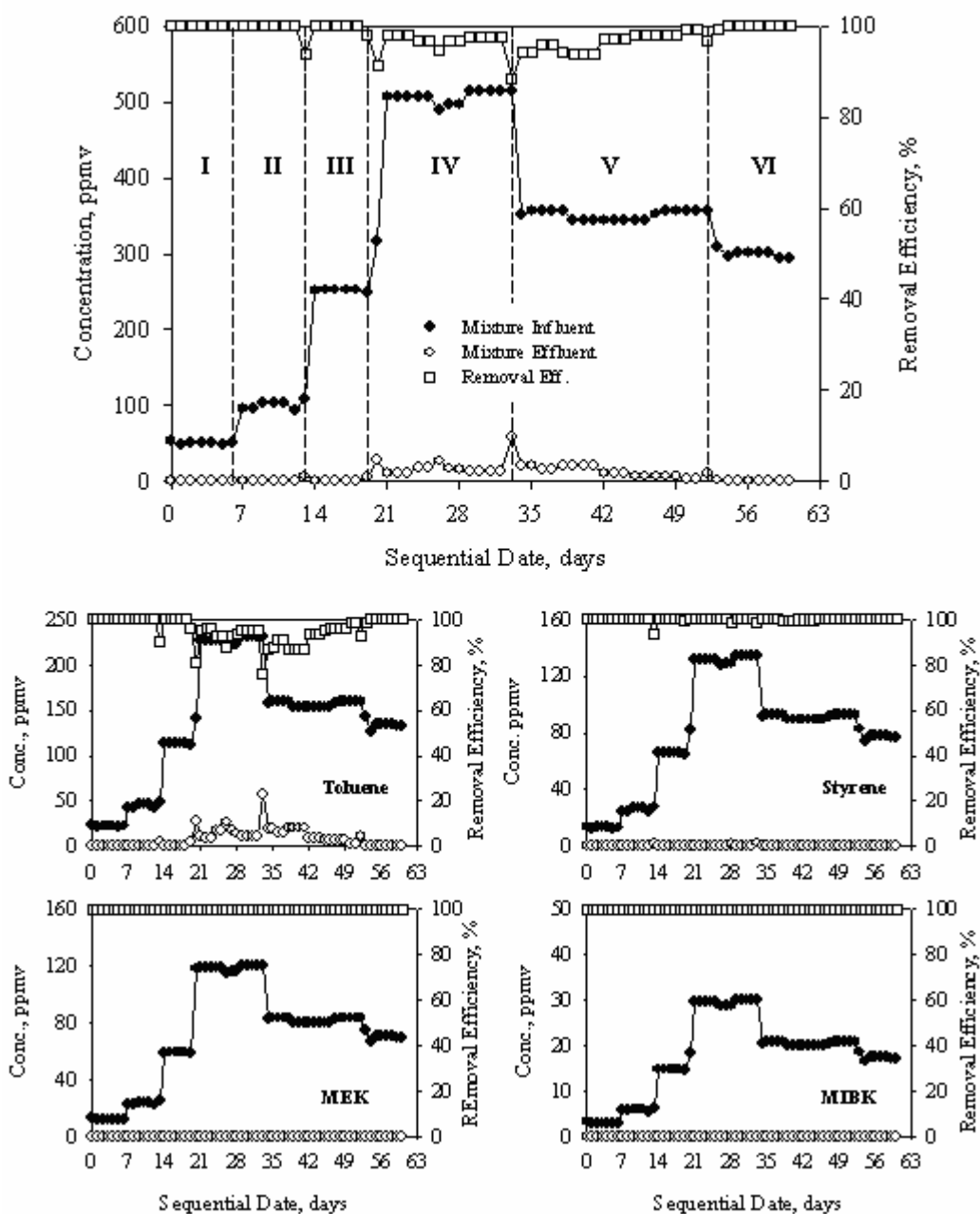


Figure 2. Performance of “Mixture 2” biofilter.

the four VOC components in the mixture (data not shown) showed that MEK and MIBK were removed completely in the upper 3/8 media depth of the two biofilters without significant difference between the two mixtures. While the biofilter depth utilization for the removal of styrene and toluene increased with increase of influent concentrations for both biofilters, which could be contributed to the required longer time for styrene and toluene to be transferred to the aqueous phase from the gas phase as compared to MEK and MIBK. Styrene removal along the biofilter depth did not have significant difference between the two mixtures due to similar styrene loading rates for

both mixtures. However, the removal of toluene in “Mixture 2” biofilter utilized more biofilter depth than that for “Mixture 1” biofilter due to higher toluene loading in “Mixture 2” biofilter.

Conclusions

This study investigated biofilter performance on two VOC mixtures. Performance with step change in VOC concentrations, biofilter re-acclimation, and media depth utilization revealed the following:

- (1) Over 99% removal efficiency could be maintained at inlet concentrations up to 500 ppmv

Table 3. Biofilter Recovery of the Removal Efficiency after Backwashing

Removal Efficiency, %									
"Mixture 1" Biofilter									
Time/min	30	60	90	120	180	300	360	1200	2880
50 ppmv	86.8	95.3	-	98.8	99.9	99.9	99.9	99.9	99.9
100 ppmv	84.5	89.2	89.2	92.6	96.9	99.9	99.9	99.9	99.9
250 ppmv	88.8	86.6	82.8	87.5	96.1	99.9	99.9	99.9	99.9
500 ppmv	80.6	84.0	79.0	81.7	93.3	98.6	99.9	99.9	99.9
1000 ppmv	79.0	80.3	73.0	72.5	79.4	80.6	81.3	81.7	80.5
"Mixture 2" Biofilter									
Time/min	30	60	90	120	180	300	360	1200	2880
50 ppmv	82.7	93.6	-	95.6	96.4	97.5	99.8	99.9	99.9
100 ppmv	77.7	88.4	-	90.4	92.7	95.2	99.9	99.9	99.9
250 ppmv	75.9	82.2	84.6	-	87.7	93.1	98.5	99.9	99.9
300 ppmv	74.9	80.2	-	-	88.1	91.9	95.0	99.8	99.9
350 ppmv	72.1	68.8	81.4	83.7	86.1	89.2	94.2	95.4	96.1
500 ppmv	71.4	74.9	79.4	-	83.4	86.7	90.0	87.8	91.3

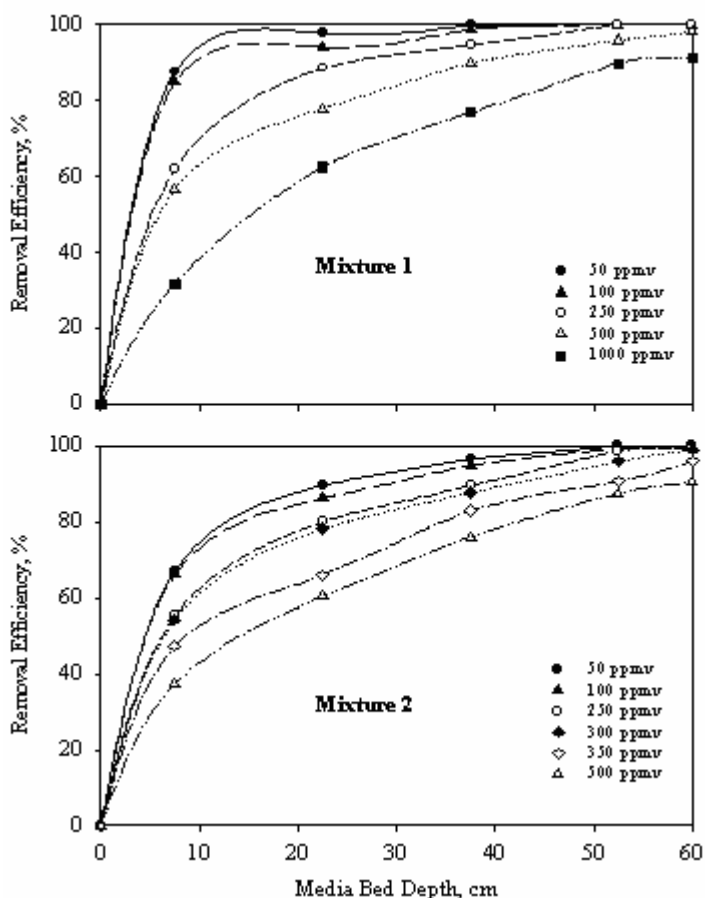


Figure 3. VOC removal along biofilter depth.

(loading rate 3.94 kg COD/m³.day) and 300 ppmv (loading rate 2.41 kg COD/m³.day) for the equimolar ratio mixture ("Mixture 1" biofilter) and typical ratio mixture based on point source air emission ("Mixture 2" biofilter), respectively.

(2) Re-acclimation was delayed for both mixtures with increase of inlet concentrations. The biofilter performance for mixture 2 required longer time to recover than that mixture 1 due to higher toluene content in mixture 2.

- (3) Biofilter depth utilization increased with increase of inlet 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.
- (4) Toluene content in the mixture played a major role in the biofilter overall performance.

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