Removal of Methyl Isobutyl Ketone From Contaminated Air by Trickle-Bed Air Biofilter

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Abstract: A laboratory-scale trickle-bed air biofilter was evaluated for the removal of methyl isobutyl ketone (MIBK) from a waste gas stream. Six-millimeter (6 mm) Celite pellets (R-635) were used as the biological attachment medium. Effects of MIBK volumetric loading rates on removal efficiency, biofilter reacclimation, biomass growth, and removal kinetics were studied under three different operating conditions, namely, backwashing and two intermittent periods (off chemical—no MIBK input; and off flow-no flow input). Backwashing of the biofilter once a week with full-medium fluidization removed the excess biomass and attained stable long-term performance with over 99% removal efficiency for loading rates less than 3.26 kg chemical oxygen demand (COD)/m^3 day. The two intermittent periods could also sustain high removal efficiency for loading rates up to 1.09 kg COD/m^3 day without any backwashing. The recovery time increased with an increase in loading rates. Furthermore, the intermittent operations required a longer time to recover than backwashing. The pseudo-first-order removal rate constant decreased with an increase in volumetric loading rate. The removal kinetics showed an apparent dependency on the experimental operating conditions.

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CE Database subject headings: Biomass; Biodegradation; Biological treatment; Biofilm; Gas; Volatile organic compounds; Backwashing; Fixed-bed operations.

Introduction

The Clean Air Act Amendments of 1990 require maximum achievable control technology standards for 189 hazardous air pollutants (Lee 1991). Many of these pollutants are volatile organic compounds (VOCs) that are of environmental concern due to their toxicity. 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.

Biofilter performance for VOCs control is strongly affected by the type of packing materials (media) used for microbial attachment. Biofilter media are mainly of two types: Natural organic media and inert synthetic media. The synthetic media biofilter is usually referred to as a trickle-bed air biofilter (TBAB). TBABs facilitate more consistent operation than natural media biofilters do via better control of overall pressure drop, nutrient concentration, and pH. Furthermore, they do not suffer from the effects of aging as do natural media. A pelletized medium as biological support media has been demonstrated to be significantly superior to other media (Sorial et al. 1993a). The main disadvantage of the pelletized medium is clogging due to excessive biomass formation and retention. Procedures for limiting excess biomass accumulation without an adverse effect on the microbial effectiveness of a biofilter were investigated in previous studies (Sorial et al. 1994, 1995, 1998, Smith et al. 1998; Jorio et al. 2000).

The number of studies concerning the treatment of contaminated gas stream by TBABs has increased in the past decade (Sorial et al. 1993a,b, 1994, 1995; Zhu et al. 1996; Alonso et al. 1997, 1998, 1999, 2000, 2001; Chou and Huang 1997; Pedersen and Arvin 1997; Kong et al. 2001; Seignez et al. 2002; Smith et al. 2002; Arulneyam and Swaminathan 2003). 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. Mostly one, or a few of the affecting factors under continuous and/or constant volumetric loading rate or influent contaminant concentration, was investigated. However, few studies have been conducted on intermittent operations. Togna and Frisch (1993) reported styrene reacclimation periods after two or more days without chemical contact. Martin and Loehr (1996) reported biofilter reacclimation after restartup from two intermittent periods.

Methyl isobutyl ketone (MIBK) is a common solvent used for manufacturing paints, rubbers, pharmaceuticals, chemicals, and machinery. The typical toxicity effects of MIBK in humans exposed at 50 to 100 ppm are mucous membrane irritation and weak effects on the central nervous system (Kawai et al. 2003). Effects on the kidneys were reported after exposure at 1,000 ppm (Phillips et al. 1987).

Reports on the biofiltration of MIBK are very scarce. Deshusses et al. (1995a,b) studied the transient mass balances and

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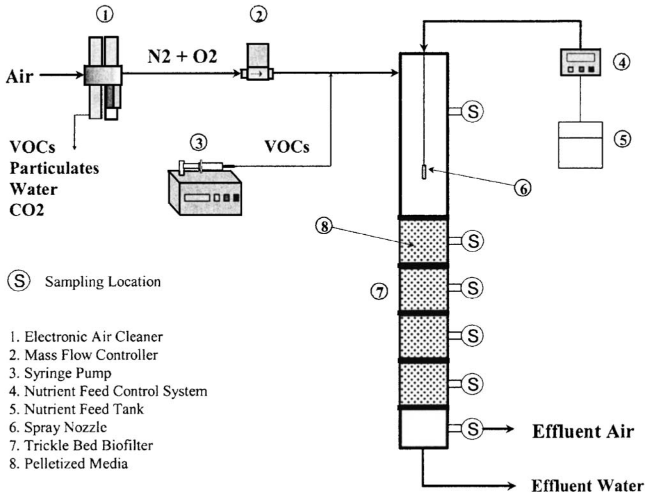

Fig. 1. Schematic of the biofiltration system

developed a novel diffusion reaction model by employing MIBK and methyl ethyl ketone (MEK) as the target contaminants in an equivolume mixture of compost and polystyrene spheres biofilter unit. In a later study, Deshusses et al. (1996) investigated the transient-state behavior of a biofilter removing mixtures of MEK and MIBK from air. Deshusses (1997) further studied the transient behavior of biofilters during startup and the interaction between pollutants in a horse manure, yard waste compost, and redwood chips mixture biofilter unit. Deshusses and Johnson (2000) used a mixture of mushroom compost and wood chips media and obtained an MIBK elimination capacity of 40–50 g/m^3 h. Aizpuru et al. (2001) used a peat biofilter for the removal of MIBK. No studies have been reported on the use of TBAB for MIBK control.

The objectives of this research were to investigate the performance of a TBAB for MIBK removal under organic loading rates up to 5.43 kg chemical oxygen demand $(COD)/m^3$ day and EBRT as low as 0.76 min. The goal was to maintain consistently high removal efficiencies for long-term operation. The evaluations are focused on the following operational parameters: (1) MIBK loading; (2) recovery of biofilter performance after backwashing; (3) recovery of biofilter performance after intermittent operation; (4) recovery of biofilter performance after a change in loading rate; (5) removal efficiency with biofilter depth under steady-state conditions and development of preliminary kinetic data; and (6) CO_2 (carbon mass balance) closures.

Materials and Methods

Experimental Apparatus

The laboratory-scale biofilter system was similar to that described by Sorial et al. (1995) and Smith et al. (1996). An illustration of the biofilter system is provided in Fig. 1. The biofilter is constructed of seven cylindrical glass sections (Ace Glass Inc., Vineland, N.J.) with an internal diameter of 76 mm and a total length of 130 cm. The biofilter is equipped with sampling ports to allow sampling of the stream entering and leaving the biofilter, as well as axially along the medium bed. The biofilter is packed with pelletized diatomaceous earth biological support media (Celite 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, Calif.) to a depth of about 60 cm. The properties of the pellets are provided in Smith et al. (1996). The biofilter was operated at a constant temperature of 20°C and in a co-current gas and liquid downward flow mode.

The air supplied to the biofilter is purified by the complete removal of water, oil, carbon dioxide, VOCs, and particulates. The air pressure is reduced to 20 psig (140 kPa) by a pressure control valve. The air flow to the biofilter is set up at the rate of 3.6 L/min. Liquid VOC was injected via a syringe pump (Harvard Apparatus, model NP 70-2208, Holliston, Mass.) into the air stream where it vaporized, and entered the biofilter through the topmost side port of the column.

The biofilter is equipped with an independent system for intermittently feeding 1.5 L/day of a buffered nutrient solution through a misting nozzle (Corrigan Corporation, Northbrook, Ill.), according to a formulation described by Sorial et al. (1995). A spike solution of 2 M $NaNO_3$, and 0.22 M NaH_2PO_4 was added to the nutrient feed solution to maintain a COD-to-nitrogen ratio of 50:1 and a nitrogen-to-phosphorous mass ratio of 4:1. $NaHCO_3$ was used as a pH buffer. The sole source of nutrient-nitrogen, nitrate (NO_3-N) is used because the use of nitrate (NO_3-N) instead of ammonia (NH_3-N) is effective in reducing the observed biomass yield and provided better biofilter performance (Smith et al. 1996).

Microbial Seed

The biofilter was initially seeded with an aerobic microbial culture, which was obtained from the secondary clarifier of an activated sludge system at a municipal wastewater treatment plant (Millcreek Wastewater Treatment Plant, Cincinnati, Ohio).

Experimental Plan

Comprehensive investigations were conducted on the biofilter system for five different employed loading rates from 1.09 to 5.43 kg COD/m^3 day. For each employed loading rate, three operating conditions were conducted, namely, backwashing and two intermittent operations (off chemical and off flow).

Backwashing Operating Condition

The backwashing was conducted while the biofilter was shut off by recycling 18 L of the buffered nutrient solution to fluidize the media for a defined time period. Finally, the recycle was shut off and another 18 L of the buffered nutrient solution was passed through the column as a rinse. The backwashing duration and frequency were initially set at a 1 h duration per week for a period of 3 weeks for each loading rate (if necessary, the backwash duration was extended to 2 h). Compressed air was introduced, if necessary, to help break up and scour the media.

Off Chemical Operating Condition

This experimental condition involves the period without MIBK loading, i.e., pure air with nutrient flow through the biofilter. The duration and frequency for this operating condition were 2 days per week for a period of 3 weeks at MIBK loadings of 1.09, 2.17, and 5.43 kg COD/m^3 day.

Off Flow Operating Condition

This experimental condition reflects no flow, i.e., no nutrients and air flows passing through the biofilter. The duration and frequency for this operating condition were 2 days per week for a period of 3 weeks at MIBK loadings of 1.09, 2.17, and 5.43 kg COD/m^3 day.

Table 1. Experimental Operating Conditions

	a	b	c	d	e
Experimental conditions					
Inlet concentration (ppmv)	50	100	250	200	150
Loading rate (kg COD/m^3 day)	1.09	2.17	5.43	4.34	3.26
EBRT (min)	0.76	0.76	0.76	0.76	0.76
Operating periods in days					
Backwashing	1–29	69–85	125–169	216–244	245–309
Intermittent period					
Off chemical (2 days/week)	30–50	86–106	170–190	—	—
Off flow (2 days/week)	51–68	107–124	191–215	—	—

Note: EBRT=empty bed retention time and COD=chemical oxygen demand.

Materials

The MIBK used in this study was reagent grade 99.5% purity (Fisher Scientific, Fair Lawn, N.J.).

Analytical Methods

The concentrations of MIBK in the gas phase were measured by chromatographic separation on a 30 m length, 0.25 mm inner diameter, 0.25 μm film narrowbore column (DB 624, J and W Scientific, Folsom, Calif.) using a gas chromatograph (GC) (HP 5890, Series II, Hewlett-Packard, Palo Alto, Calif.) equipped with a flame ionization detector (FID). The GC oven temperature was programmed from 40 to 120°C at rate of 10°C/min with a 2 min hold at 40°C and a 2 min hold at 120°C. The carrier gas (N_2) flow rate was set at 2.3 mL/min. The FID detector was used with N_2 make-up gas at a flow rate of 20 mL/min, a fuel gas flow (H_2) of 30 mL/min, and an oxidizing gas flow (air) of 300 mL/min. The detector temperature was 250°C. The retention time for MIBK was 3.1 min under the conditions used.

Effluent gas phase samples for CO_2 analysis were also taken by using gas-tight syringes through sampling ports in the biofilter. A GC equipped with a thermal conductivity detector (TCD) was used for determining the CO_2 concentrations in the effluent gas phase. The GC oven temperature was programmed from 50 to 80°C at 10°C/min with a 3.2 min hold at 50°C and a 1.5 min hold at 80°C. The carrier gas (He) flow rate was set at 30 mL/min, and the TCD detector was used with a He make-up gas at a flow rate of 35 mL/min.

Liquid phase samples were analyzed for $NO_3^-{-}N$, total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. $NO_3^-{-}N$ was determined according to Standard Methods 4500$-NO_3^-$ B (APHA/AWWA/WEF 1998) by using a Shimadzu UVmini 1240 ultraviolet-visible spectrophotometer (Shimadzu Corp., Tokyo, Japan). Samples were filtered through 0.45 μm nylon filters (Micron Separation, Westboro, Mass.) prior to analysis. TC and IC were determined by using a Shimadzu TOC 5050 analyzer (Shimadzu Corp., Tokyo, Japan) according to Standard Methods 5310 (APHA/AWWA/WEF 1998). The VSS concentrations in the effluent and backwashing water were determined according to Standard Methods 2540 G (APHA/AWWA/WEF 1998). pH was determined using a Fisher Accumet pH meter, Model 50 (Fisher Scientific Co., Inc., Fair Lawn, N.J.). Pressure drop along the biofilters was monitored by a digital manometer (Modus Instruments, Inc., Clinton, Mass.).

Results and Discussion

Biofilter Performance

The biofilter was started up at a 50 ppmv MIBK inlet concentration with a corresponding loading of 1.09 kg COD/m^3 day, 0.76 min EBRT, and 3.75 mmol $NO_3^-{-}N$/day. The operating conditions are summarized in Table 1. The biofilter performance with respect to MIBK removal at different loading rates is given in Fig. 2. In Stage a, the overall removal efficiency had reached over 90% by Day 6, and after about 14 days from the start-up period, the biofilter maintained a consistently high removal efficiency above 99%. This efficiency was maintained for all the three experimental operating conditions (backwashing and the two intermittent periods).

On Day 69, the MIBK biofilter was backwashed, and the inlet concentration was increased to 100 ppmv with a corresponding loading of 2.17 kg COD/m^3 day (Stage b). The $NO_3{-}N$ feed rate was increased correspondingly to 7.50 mmol/day. No apparent acclimation period to the new higher loading rate was observed. The biofilter maintained a stable long-term removal efficiency above 99% for the duration of the backwashing and off chemical operating conditions. While for the off flow operating condition, after the first cycle of off flow was conducted, the biofilter recovered to 99% removal efficiency within 30 min and maintained this removal level till the third day. On the fourth day, the overall

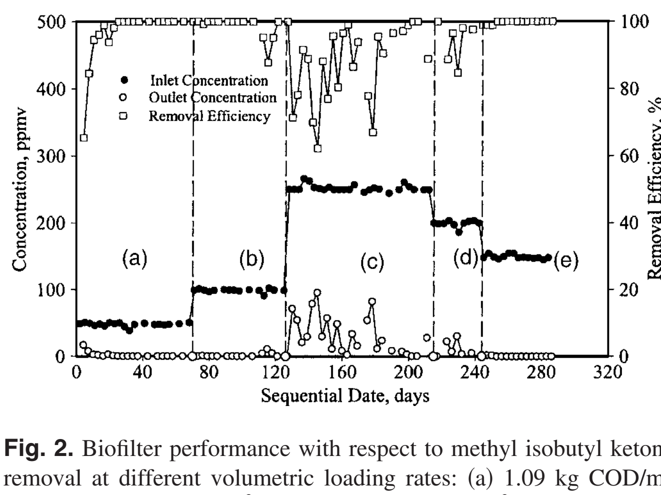

Fig. 2. Biofilter performance with respect to methyl isobutyl ketone removal at different volumetric loading rates: (a) 1.09 kg COD/m^3 day; (b) 2.17 kg COD/m^3 day; (c) 5.43 kg COD/m^3 day; (d) 4.34 kg COD/m^3 day; and (e) 3.26 kg COD/m^3 day

Table 2. Summary of Methyl Isobutyl Ketone Maximum Elimination Capacity (EC_{max}) and Critical Load Compared with Previously Values Observed by Others

Reference	Media	Loading rate (g/m^3 h)	EC_{max} (g/m^3 h)	Critical load (g/m^3 h)
Deshusses et al. (1995b)	An equivolume mixture of compost and polystyrene spheres	5–120 (0.33–7.80)	25–30 (1.63–1.96)	15–18 (0.99–1.20)
Deshusses and Johnson (2000)	A mixture of mushroom compost and wood chips	—	40–50 (2.61–3.26)	13–15 (0.85–0.99)
Aizpuru et al. (2001)	Peat	5–20 (0.33–1.31)	10–12 (0.66–0.78)	10 (0.66)
Current study	Pelletized diatomaceous earth biological support media	17–84 (1.09–5.43)	73 (4.80)	50 (3.30)

Note: The value in parentheses represents the loading rate in kg COD/m^3 day.

removal efficiency decreased to 95%, and on the sixth day, dropped further to 88%. It had been observed that the bed media were dark brown and had lots of black spots, indicating that the biofilter performance decreased substantially due to the accumulation of excess biomass. This behavior indicated that the excess biomass was still held within the system and was causing channeling or short circuiting. Backwashing was, therefore, conducted in the second off flow cycle for removing the excess accumulated biomass in the biofilter. The biofilter recovered to the 99% removal level after backwashing and maintained this level during the third cycle of off flow.

On Day 125 after backwashing, the inlet concentration was increased to 250 ppmv with a corresponding loading of 5.43 kg COD/m^3 day (Stage c). The NO_3^-–N feed rate was increased accordingly to 22.5 mmol/day. After the increase of inlet concentration, the removal efficiency increased to 92% and decreased to 62% prior to the next backwashing. At the same time, it was found that due to the high consumption of the NO_3^-–N, more amounts were needed to maintain the microbial activity. The feed rate was then increased gradually to 52.5 mmol/day by Day 152. During the backwashing operating condition, the biofilter recovered to the 99% removal efficiency level just after backwashing, then, its efficiency decreased gradually to around 80% removal just prior to the next backwashing period. During the intermittent operations, in order to improve the overall removal efficiency, backwashing was employed as the active biomass control. However, the biofilter could not maintain the 99% removal level; it decreased to around 70% removal efficiency just prior to the next backwashing. It was also found that more feed NO_3^-–N was required (105 mmol/day) to maintain the microbial activity for the intermittent operations. It is speculated that the intermittent period at the current MIBK loading could not maintain efficient biomass control. In order to achieve stable long-term removal efficiency above 99% at this loading rate, backwashing should be conducted more frequently. Therefore, lower MIBK loading rates were employed in the following experiments.

In order to determine the maximum loading rate that will provide stable 99% removal efficiency under weekly backwashing, on Day 216 after backwashing, the inlet concentration was decreased to 200 ppmv with a corresponding loading of 4.34 kg COD/m^3 day (Stage d). Although the overall removal efficiency increased to 95% for three backwashing cycles, it could not be maintained at 99% removal level. On Day 245 after backwashing, the inlet concentration was decreased further to 150 ppmv with a corresponding loading of 3.26 kg COD/m^3 day (Stage e). The removal efficiency recovered to the 99% level in 60 min after backwashing and could be sustained over 99% during the whole backwashing cycles.

The results obtained from this study and those reported by other authors are summarized in Table 2. The maximum elimination capacity (EC_{max}) is defined as the maximum capacity that can be removed regardless of the employed loading rates. The critical loading is defined as the maximum loading beyond which the removal deviates significantly from the 100% removal line (Deshusses and Johnson 2000). It can be deduced from Table 2 that the MIBK biofilter in this study exceeded any reported elimination capacity. The higher EC_{max} and critical loading were mainly due to the superior employed pelletized diatomaceous earth biological support media and the efficient biomass control operating conditions. The elimination capacity with respect to loading rate is presented in Fig. 3. Fig. 3 indicates that the maximum elimination capacity of MIBK studied in our biofilter system is 4.8 kg COD/m^3 day, and the critical load is 3.3 kg COD/m^3 day.

Biofilter Response after Backwashing and Intermittent Periods

Effluent samples were collected at prescheduled intervals to evaluate the biofilter response subsequent to backwashing and intermittent periods. Fig. 4 shows the effluent response corresponding to backwashing operation and two intermittent operations for employed MIBK loading rates of 1.09, 2.17, and 5.43 kg COD/m^3 day and backwashing only for loading rates of 3.26 and 4.34 kg COD/m^3 day. Due to the high biomass accumulation for 5.43 kg COD/m^3 day loading rate, backwashing was also employed for off chemical and off flow operation.

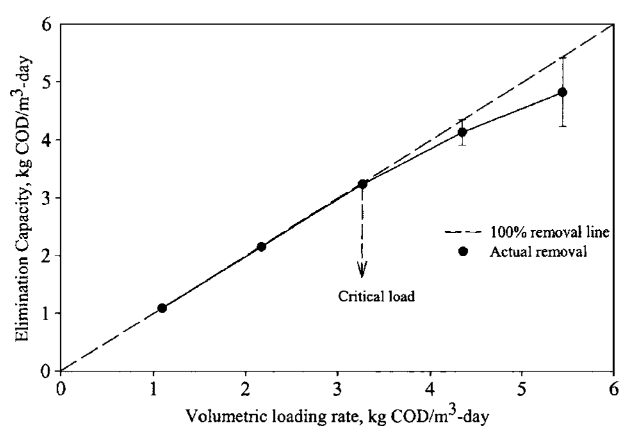

Fig. 3. Elimination capacity with respect to loading rate

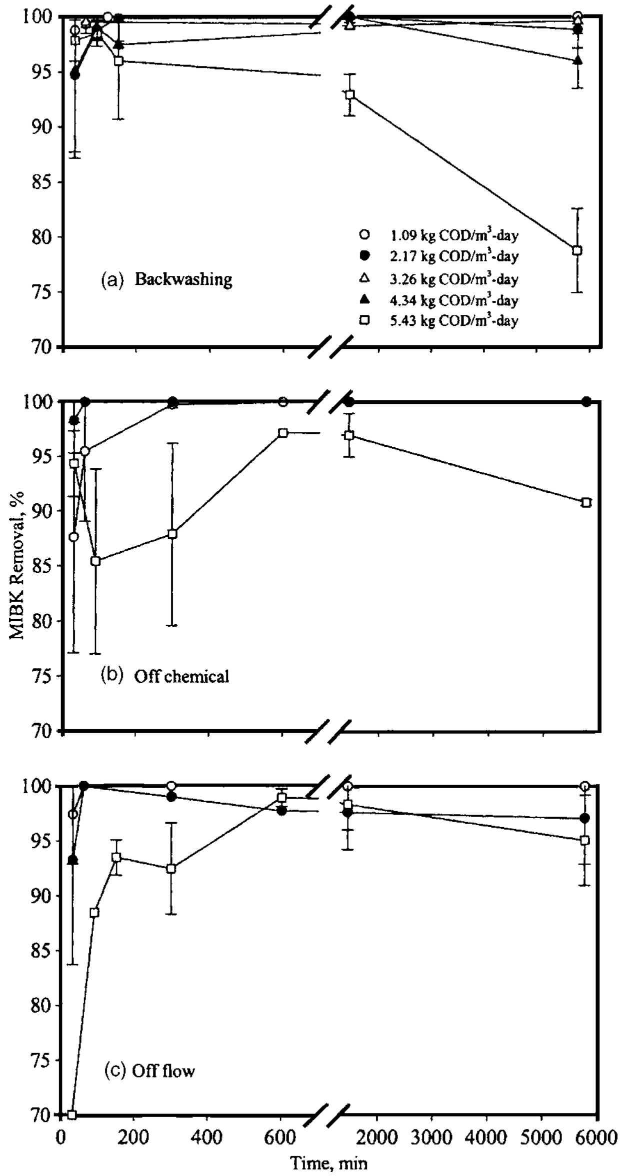

Fig. 4. Effluent response corresponding to the backwashing and intermittent periods for different methyl isobutyl ketone (MIBK) loadings

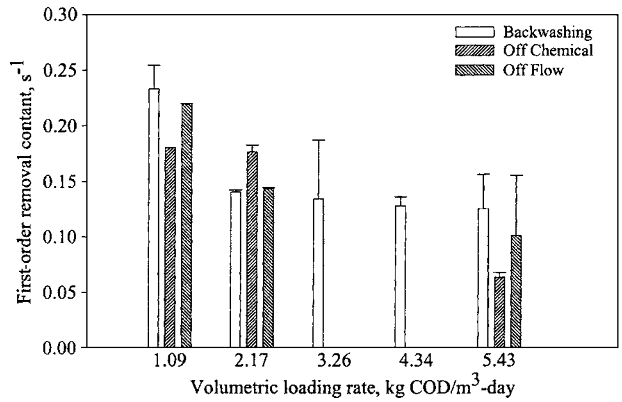

Fig. 5. Reaction rate for the three different operating conditions

Reacclimation was considered to have been achieved when 99% of the original biofilter performance was attained.

It can be deduced from Fig. 4 that the reacclimation of biofilter was delayed as the employed loading rate was increased. For loading rate of 1.09 kg COD/m^3 day, reacclimation had no apparent difference between the backwashing operating condition and the two intermittent operations. The results at 1.09 kg COD/m^3 day loading rate are speculated to be caused by the fact that less biomass was produced and accumulated within the biofilter. For loading rate of 2.17 kg COD/m^3 day, the intermittent operating conditions provided better reacclimation performance than the backwashing operating condition. It is speculated that the increased reacclimation difference between backwashing and intermittent operating conditions at loading rate of 2.17 kg COD/m^3 day was due to more available biomass during the intermittent operating conditions since the excess biomass in the backwash operating condition was removed during backwashing. For loading rate of 5.43 kg COD/m^3 day, no full recovery was encountered for all the three operating conditions. It is speculated that for a loading rate of 5.43 kg COD/m^3 day, channeling might have occurred due to an excess accumulation of biomass, which caused failure for complete recovery. Furthermore, the combined operation of intermittent periods and backwashing that was conducted for a 5.43 kg COD/m^3 day loading rate significantly improved the biofilter performance [see Figs. 4(b and c)].

Kinetic Analysis of Biofilter Performance

Gaseous samples were taken along the media depth of the biofilter 1 day following backwashing and intermittent periods to evaluate the biofilter performance and determine the removal kinetics. By plotting the natural logarithmic scale of the ratio of residual concentration to inlet concentration as a function of depth into the biofilter (expressed as the cumulative EBRT), i.e., $[\ln(C/C_o)\ Vst]$, the pseudo-first-order removal rate constants were obtained from the slopes of the regression lines.

Fig. 5 represents plots of the MIBK first-order removal rate constants under the different loading rates (expressed as the cumulative EBRT) for the three scenarios considered in this study. Fig. 5 indicates that the removal rate was dependent on the volumetric loading rate. The removal rate constants decreased with increase of loading rates. For loading rates of 1.09 and 5.43 kg COD/m^3 day, backwashing operating condition showed the highest removal rate constants, and the off chemical operating condition showed the lowest. It is worthwhile to note that the lower removal rate constants obtained under intermittent operating conditions for the 1.09 kg COD/m^3 day loading rate did not affect the overall biofilter performance because more biofilter depth was utilized. However, when the employed loading rate was over the critical loading rate (i.e., at 5.43 kg COD/m^3 day), the intermittent operating conditions had a significant negative effect on the biofilter performance. The biofilter performance deteriorated with time, and backwashing was deemed necessary during the intermittent periods in order to improve the biofilter performance (see subsection entitled, "*Biofilter Performance*").

At a loading rate of 2.17 kg COD/m^3 day, the off chemical operating condition showed the highest removal rate constant, and there was no apparent difference in removal rate constant between backwashing and off flow operating conditions. Since the overall performance of the biofilter was above 99% at this loading rate (see Fig. 2), the lower removal rate constants for backwashing and off flow indicates utilization of more biofilter depth.

Table 3. Statistical Analysis of g COD/g NO_3^-−N and Equivalent Volatile Suspended Solids (VSS) Yields under the Three Experimental Operating Conditions

Operating conditions	Loading rate (kg COD/m^3 day)	Feed ratio (COD/N)	g COD/g N	Standard deviation (g COD/g N)	g VSS/g COD (yield)
Backwashing	1.09	50:1	88.8	9.6	0.08
	2.17	50:1	76.5	10.3	0.09
	5.43	20:1	24.1	10.6	0.30
Off chemical	1.09	50:1	107.7	30.9	0.07
	2.17	50:1	88.1	10.3	0.08
	5.43	20:1	23.9	7.5	0.30
Off flow	1.09	50:1	72.3	16.5	0.10
	2.17	50:1	63.3	5.9	0.11
	5.43	10:1	16.9	1.6	0.42

Note: COD=chemical oxygen demand.

Nitrogen Utilization and Volatile Organic Compound Removal

Daily analyses for the influent and effluent concentrations of NO_3^-−N were conducted. The net nitrogen utilization was calculated by subtracting the amount of the NO_3^-−N species in the effluent water from the NO_3^-−N 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 stream.

Table 3 gives statistical estimates of the COD/NO_3^-−N ratio and yield (g VSS/g COD). Assuming that aerobic heterotrophic organisms accounted for the net nitrogen utilization, the ratio of COD removed to the N utilization at each of the three loading rates listed in Table 3 was calculated from the average value during the operation period of that particular loading rate for the specific experimental operating condition. The ratio of VSS produced to COD removal was estimated by assuming the VSS are 14% nitrogen. The results shown in Table 3 indicate that for loading rates 1.09 and 2.17 kg COD/m^3 day when the feed ratio of COD:N was maintained at 50:1, the three experimental operating conditions provided similar ratios of COD removed to the N utilization except for the off chemical operating condition at 1.09 kg COD/m^3 day. For 5.43 kg COD/m^3 day when the feed ratio of COD:N was 20:1, the backwashing and off chemical operating conditions provided the same ratio of COD removed to the N utilization. In case of the off flow operating condition at a loading rate of 5.43 kg COD/m^3 day, the feed COD:N was increased to 10:1 due to consumption of nitrate. Hence, the ratio of COD removal to nitrogen utilized was apparently higher than the other two operating conditions. This indicates that an increase in the feed NO_3^-−N might have caused more biomass growth. This is confirmed by the high value of yield (g VSS/g COD) (see Table 3). It is speculated that the intermittent operating conditions did not have significant effect on the yields as compared to backwashing when the same feed ratios of COD:N were maintained for the three operating conditions. It is noticed from Table 3 that lower feed ratios of COD:N lead to higher yields, which eventually provided more biomass that lead to poor biofilter performance (see Fig. 2, Stage c).

Fig. 6 shows COD/N ratios plotted against the sequential date. The ratios show apparent dependency on the employed loading rate and time at a loading rate of 1.09 kg COD/m^3 day. As the employed loading rate was increased, the ratio of COD/N decreased and was apparently independent on time within a particular loading rate. Furthermore, for any particular cycle, a high value of the ratio was noticed one day after the restart up, and then the value decreased with time to almost an asymptotic value. It is speculated that when the loading rate is low, aerobic heterotrophs degrade most MIBK contaminants by using a MIBK carbon source for growing during the earlier stage in a particular cycle, and later the heterotrophs degrade most MIBK contaminants by a using MIBK carbon source as an energy source for maintaining microbial viability. But, when the MIBK loading rate is relatively high, the time for aerobic heterotrophs to grow in the biofilter becomes short. Thus, at higher MIBK loading rates, less variation of COD/N ratio with time was observed. The utilization of MIBK for an energy source by these micro-organisms might dominate during these operating cycles.

CO_2 Closure (Carbon Mass Balance)

The cumulative CO_2 equivalent of MIBK consumed during all experimental runs was compared to the cumulative CO_2 produced within the biofilter (Fig. 7). The inlet (or outlet) cumulative CO_2 was estimated as the total cumulative CO_2 in the influent (or effluent) aqueous and gaseous stream. The outlet cumulative CO_2 was about 94.3% of the inlet cumulative CO_2 at the end of

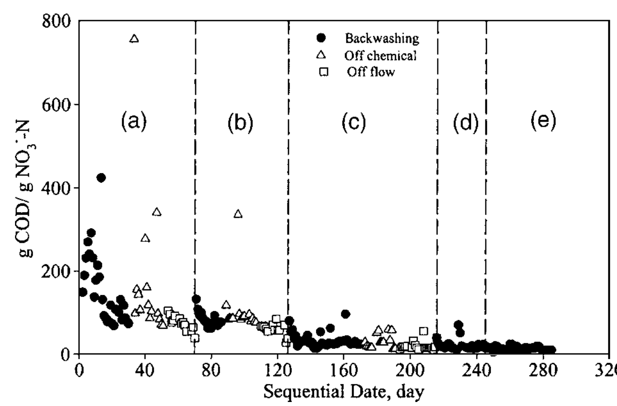

Fig. 6. g COD/g NO_3^-−N with respect to time [loading rate: (a) 1.09 kg COD/m^3 day; (b) 2.17 kg COD/m^3 day; (c) 5.43 kg COD/m^3 day; (d) 4.34 kg COD/m^3 day; and (e) 3.26 1.09 kg COD/m^3 day]

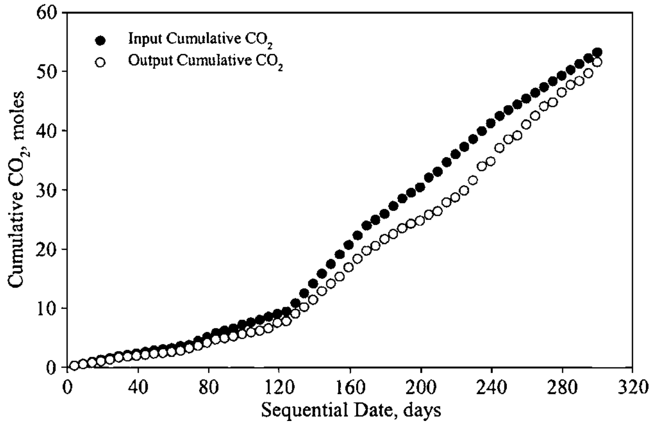

Fig. 7. Development of biofilter with time (CO_2 closure)

experiment. It is seen from Fig. 7 that there is very good closure between the two cumulative values up to Day 130 which corresponds to the commencement of 5.43 kg COD/m^3 day loading rate (Day 125), and then the two cumulative values started to deviate. The two cumulative values started to approach each other again from Day 240, which corresponds to the commencement of 3.26 kg COD/m^3 day loading rate. It is interesting to note that the cumulative CO_2 has very good closure when the biofilter had a stable 99% removal efficiency. The closure was apparently not good when the biofilter performance started to deteriorate at the 5.43 kg COD/m^3 day loading rate. The deviations between the input cumulative CO_2 and the output cumulative CO_2 started to increase with time. These deviations could be due to unwashed biomass within the biofilter which is not accounted for and might also be due to indigenous respiration during the intermittent periods which were also not accounted.

Conclusions

This study evaluated the performance of a TBAB operated at different MIBK volumetric loading rates from 1.09 to 5.43 kg COD/m^3 day with an EBRT of 0.76 min and 1.5 L/day of nutrient solution flow. Backwashing and two intermittent operating conditions were studied. The maximum elimination capacity was determined to be 4.8 kg COD/m^3 day and the critical loading was 3.3 kg COD/m^3 day. For 1.09 and 2.17 kg COD/m^3 day loading rates, long-term stable removal efficiencies at the 99% level were attained for both backwashing and the two intermittent operating conditions. For a 5.43 kg COD/m^3 day loading rate, backwashing or the intermittent operating conditions could not achieve 99% removal efficiencies, but a combination of backwashing and intermittent operation can significantly improve the removal efficiency.

Effluent samples collected after backwashing and the intermittent operations (off chemical and off flow) revealed that the biofilter recovery was delayed with the increase in employed loading rate. The biomass growth for different loading rates caused the reacclimation difference between the backwashing and the two intermittent operating conditions. For a loading rate of 1.09 kg COD/m^3 day, reacclimation had no apparent difference for backwashing and the two intermittent operating conditions. For a loading rate of 2.17 kg COD/m^3 day, the intermittent operating conditions provided better reacclimation performance than backwashing. For a loading rate of 5.43 kg COD/m^3 day, no full recovery was encountered for all the three experimental operating conditions. Effluent samples after an increase in loading rate revealed that reacclimation can be attained if the new loading rate did not exceed the critical elimination capacity.

Analysis of samples collected along the biofilter media depth one day after backwashing and intermittent operations revealed that the utilized depth of the biofilter increased with an increase in MIBK loading rate and the apparent removal rate constant decreased with an increase in MIBK loading rate. The three experimental operating conditions used in this study had different effects on the removal kinetics for the employed MIBK loading rates. For loading rates of 1.09 and 5.43 kg COD/m^3 day, the backwashing operating condition showed the highest removal rates, and the off chemical operating condition showed the lowest rate. On the other hand, for a loading rate of 2.17 kg COD/m^3 day, the off chemical operating condition showed the highest removal rate, and there was no apparent difference in removal rates between backwashing and off flow operating conditions.

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References

Aizpuru, A., Malhautier, L., Roux, J. C., and Fanlo, J. L. (2001). "Biofiltration of a mixture of volatile organic emissions." *J. Air Waste Manage. Assoc.*, 51(12), 1662–1670.

Alonso, C. et al. (1997). "Gas treatment in trickle-bed biofilters: Biomass, how much is enough?" *Biotechnol. Bioeng.*, 54(6), 583–594.

Alonso, C., Suidan, M. T., Kim, B. R., and Kim, B. J. (1998). "Dynamic mathematical model for the biodegradation of VOCs in a biofilter: Biomass accumulation study." *Environ. Sci. Technol.*, 32(20), 3118–3123.

Alonso, C., Zhu, Y., Suidan, M. T., Kim, B. R., and Kim, B. J. (1999). "Mathematical model for the biodegradation of VOCs in trickle bed biofilters." *Water Sci. Technol.*, 39(7), 139–146.

Alonso, C., Zhu, X. Q., Suidan, M. T., Kim, B. R., and Kim, B. J. (2000). "Parameter estimation in biofilter systems." *Environ. Sci. Technol.*, 34(11), 2318–2323.

Alonso, C., Zhu, X. Q., Suidan, M. T., Kim, B. R., and Kim, B. J. (2001). "Mathematical model of biofiltration of VOCs: Effect of nitrate concentration and backwashing." *J. Environ. Eng.*, 127(7), 655–664.

American Public Health Administration, American Water Works Association, and Water Environment Federation (APHA/AWWA/WEF). (1998). *Standard methods for the examination of water and wastewater*, 20th Ed., APHA, AWWA, and WEF, Washington, D.C.

Arulneyam, D., and Swaminathan, T. (2003). "Biodegradation of methanol vapor in a biofilter." *J. Environ. Sci. (China)*, 15(5), 691–696.

Chou, M. S., and Huang, J. J. (1997). "Treatment of methylethylketone in air stream by biotrickling filters." *J. Environ. Eng.*, 123(6), 569–576.

Deshusses, M. A. (1997). "Transient behavior of biofilters: Start-up, carbon balances, and interactions between pollutants." *J. Environ.*

Eng., 123(6), 563–568.
Deshusses, M. A., Hamer, G., and Dunn, I. J. (1995a). "Behavior of biofilters for waste air biotreatment.1: Dynamic-model development." *Environ. Sci. Technol.*, 29(4), 1048–1058.
Deshusses, M. A., Hamer, G., and Dunn, I. J. (1995b). "Behavior of biofilters for waste air biotreatment.2: Experimental evaluation of a dynamic model." *Environ. Sci. Technol.*, 29(4), 1059–1068.
Deshusses, M. A., Hamer, G., and Dunn, I. J. (1996). "Transient-state behavior of a biofilter removing mixtures of vapors of MEK and MIBK from air." *Biotechnol. Bioeng.*, 49(5), 587–598.
Deshusses, M. A., and Johnson, C. T. (2000). "Development and validation of a simple protocol to rapidly determine the performance of biofilters for VOC treatment." *Environ. Sci. Technol.*, 34(3), 461–467.
Don, J. A., and Feenstra, L. (1984). "Ordor abatement through biofiltration." *Proc., Symp. on Characterization and Control of Odoriferous Pollutants in Process Industries*, Le Neuve, Belgium.
Jorio, H., Bibeau, L., and Heitz, M. (2000). "Biofiltration of air contaminated by styrene: Effect of nitrogen supply, gas flow rate, and inlet concentration." *Environ. Sci. Technol.*, 34(9), 1764–1771.
Kawai, T. et al. (2003). "Methyl isobutyl ketone and methyl ethyl ketone in urine as biological markers of occupational exposure to these solvents at low levels." *Int. Arch. Occup. Environ. Health*, 76(1), 17–23.
Kong, Z., Farhana, L., Fulthorpe, R. R., and Allen, D. G. (2001). "Treatment of volatile organic compounds in a biotrickling filter under thermophilic conditions." *Environ. Sci. Technol.*, 35(21), 4347–4352.
Lee, B. (1991). "Highlights of the clean air act amendments of 1990." *J. Air Waste Manage. Assoc.*, 41(1), 16–19.
Martin, F. J., and Loehr, R. C. (1996). "Effect of periods of non-use on biofilter performance." *J. Air Waste Manage. Assoc.*, 46(6), 539–546.
Ottengraf, S. P. P. (1986). "Exhaust gas purification." *Biotechnology*, H. J. Rehm and G. Reed, eds., VCH Verlagsgesellsch, Weinheim, Germany, 8, 425–452.
Pedersen, A. R., and Arvin, E. (1997). "Toluene removal in a biofilm reactor for waste gas treatment." *Water Sci. Technol.*, 36(1), 69–76.
Phillips, R. D. et al. (1987). "A 14-week vapor inhalation toxicity study of methyl isobutyl ketone." *Fundam. Appl. Toxicol.*, 9(3), 380–388.
Seignez, C., Atti, A., Adler, N., and Peringer, P. (2002). "Effect of biotrickling filter operating parameters on chlorobenzenes degradation." *J. Environ. Eng.*, 128(4), 360–366.
Smith, F. L. et al. (1996). "Development of two biomass control strategies for extended, stable operation of highly efficient biofilters with high toluene loadings." *Environ. Sci. Technol.*, 30(5), 1744–1751.
Smith, F. L. et al. (1998). "Evaluation of trickle bed air biofilter performance as a function of inlet VOC concentration and loading, and biomass control." *J. Air Waste Manage. Assoc.*, 48(7), 627–636.
Smith, F. L., Sorial, G. A., Suidan, M. T., Biswas, P., and Brenner, R. C. (2002). "Development and demonstration of an explicit lumped-parameter biofilter model and design equation incorporating Monod kinetics." *J. Air Waste Manage. Assoc.*, 52(2), 208–219.
Sorial, G. A. et al. (1993a). "Development of aerobic biofilter design criteria for treating VOCs." *Proc., 86th Annual Meeting and Exhibition of the Air and Waste Management Asociation*.
Sorial, G. A. et al. (1993b). "Evaluation of biofilter media for treatment of air streams containing VOCs." *Proc., Water Environment Federation 66th Annual Conf. and Exposition*, 429–439.
Sorial, G. A. et al. (1994). "Evaluation of performance of trickle bed biofilter-impact of periodic removal of accumulated biomass." *Proc., 87th Annual Meeting and Exhibition of the Air and Waste Management Association*.
Sorial, G. A., Smith, F. L., Suidan, M. T., Biswas, P., and Brenner, R. C. (1995). "Evaluation of trickle-bed biofiltermedia for toluene removal." *J. Air Waste Manage. Assoc.*, 45(10), 801–810.
Sorial, G. A. et al. (1998). "Evaluation of trickle-bed air biofilter performance for styrene removal." *Water Res.*, 32(5), 1593–1603.
Togna, A. P., and Frisch, S. (1993). "Field-pilot study of styrene biodegradation using biofiltration." *Proc., 86th Annual Meeting and Exhibition of the Air and Waste Management Association*.
Zhu, X., Rihn, M. J., Suidan, M. T., Kim, B. J., and Kim, B. R. (1996). "The effect of nitrate on VOC removal in trickle bed biofilters." *Water Sci. Technol.*, 34(3–4), 573–581.