Chemical Engineering Journal 151 (2009) 105–112

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Treatment of dynamic VOC mixture in a trickling-bed air biofilter integrated with cyclic adsorption/desorption beds

Zhangli Cai[a], George A. Sorial[b,*]

[a] Metcalf & Eddy, 135 Merchant Street, Suite 160, Cincinnati, OH 45246, USA
[b] Dept. of Civil and Environmental Engineering, Univ. of Cincinnati, 765 Baldwin Hall, Mail Location 0071, Cincinnati, OH 45221, USA

ARTICLE INFO

Article history:
Received 18 August 2008
Received in revised form 5 February 2009
Accepted 6 February 2009

Keywords:
Adsorption
Cyclic adsorption/desorption beds
Biofiltration
Bioremediation
Trickling-bed air biofilter
VOCs

ABSTRACT

A dual-fixed adsorption system involving a two-step cycle, i.e., adsorption and desorption was evaluated for dampening load fluctuation of a mixture of volatile organic compounds (VOCs)—toluene, styrene, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK). The cyclic beds successfully performed its function as a buffering unit for the fluctuating inlet loadings. When the employed loading did not exceed the critical loading of 34.0 g/(m^3 h), the integrated system maintained consistent 99% removal efficiency regardless of the fluctuation in feeding conditions prior to the cyclic adsorption beds. However, the performance of a standalone biofilter (control biofilter) fluctuated with the fluctuation of the feeding conditions. Under loadings exceeding the critical loading capacity, the integrated system showed much higher and more stable performance than the control system although it could not maintain consistent 99% removal efficiency. The cyclic beds could also act as a feeding source during starvation periods of the system which greatly enhanced the re-acclimation time for the biofilter and at the same time will regenerate the adsorber beds.

1. Introduction

Volatile organic compounds (VOCs) are major contaminants in waste gas. USA air emissions amounted to about 0.6 Mt of pollutants in 2006 which corresponded to 33.1% of the total release of pollutants in the environment (air, land, water, and underground injection) [1]. Several physical-chemical technologies including condensation, incineration, absorption/stripping, adsorption, and catalytic combustion have been used to remove VOCs from gaseous streams, however, these technologies are either costly or they convert the VOC from the gas phase to another phase. Biofiltration systems have recently emerged as an efficient and cost-effective technology for the control of VOCs emission. This technology has been used in Europe for many years and is considered to be a best available control technology (BACT) for treating contaminated gaseous streams. Biofilters function efficiently and economically for removing low concentrations of VOCs and odor.

Several studies have been conducted on VOCs removal through biofiltration systems since the 1990s [2–7]. Factors affecting the decontamination efficiency were the nature of the contaminants, packing materials and configurations, empty bed retention time (EBRT), volumetric loading rates, nutrient feed flow rates, nutrient solution pH, and air flow patterns. Most reported studies were conducted on single solute VOC and performed in bench, pilot, or pilot-field scale reactors. Studies on VOCs mixture for biofiltration are relatively scarce [8–13].

Fluctuations in concentration and variation in the waste air composition are most commonly encountered in the chemical industry, which challenges the application of biofiltration technology. One approach for reducing the loading fluctuation to the biofilters is by installing activated carbon (AC) bed as buffer unit before the biofilter. When the system is during periods of high VOC loading, the AC bed will act as adsorption unit to accumulate VOCs. When the system is during periods of low VOC loading, the AC bed will release accumulated VOCs. In this manner, the AC bed could dampen fluctuations in loading to the biofilter and help maintain long-term consistent performance for the biofilter. Although this strategy was first proposed by Ottengraf [14] in 1986, experimental testing on this system is very limited [15–17]. Moe and Li [16] tested toluene load equalization effect by adsorption columns packed with granular activated carbon (GAC) under intermittent loading scenario. The intermittent loading conditions consisted of 8 h contaminant loading followed by 16 h non-loading each day. They found that the GAC columns could successfully achieve load equalization of toluene contaminated air streams. Degree of load attenuation became more pronounced at lower contaminant concentrations and higher GAC empty bed contact times (EBCTs). Weber and Hartmans [17] tested the buffer capacity of a number of activated carbons to a followed biofilter packed with compost and polystyrene with fluctuating

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[*] Corresponding author. Tel.: +1 513 556 2987; fax: +1 513 556 2599.
E-mail addresses: Zhangli.Cai@m-e.aecom.com (Z. Cai), George.Sorial@uc.edu (G.A. Sorial).

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doi:10.1016/j.cej.2009.02.002

concentrations of toluene. They found that the toluene fluctuations could be decreased to around 300 mg m^{-3} when the fluctuations were between 0 and 1000 mg m^{-3}.

In practice, the buffer capacity of a single bed adsorption will be quickly exhausted if larger contaminant continuous loading fluctuations are encountered. Furthermore, it could cause a starvation period within the biofilter during the initial start-up period due to adsorption until breakthrough. To overcome the difficulty of a single bed buffer unit, a 2-bed adsorption unit with cyclic adsorption and desorption was proposed and applied as a buffer unit for the dampening fluctuating feed condition to the followed biofilter in this study. The idea of the cyclic 2-bed adsorption was inspired by the basic concept of pressure swing adsorption (PSA). PSA is a cyclic process used to selectively adsorb and separate components of a feed gas mixture, thereby producing partially purified gas products [18,19]. A typical PSA cycle includes four steps: pressurization, adsorption, depressurization, and regeneration [20]. The cyclic operation in adsorption and regeneration (desorption) has the potential to attenuate the fluctuation in feeding loads.

An integrated system of a 2-bed cyclic adsorption/desorption unit and trickle bed air biofilter (TBAB) was tested in our previous study for removal of fluctuating toluene concentrations from the gas phase [21]. The integrated system proved to dampen the toluene feeding fluctuation. The primary objective of this study is, therefore, to extend the application of the integrated technology to the multicomponent system. The evaluations are focused on the following aspects: (1) evaluation of the buffering capacity of the cyclic 2-bed adsorption unit and comparing its performance to a stand-alone biofilter, (2) carbon mass balance closures, and (3) development of preliminary kinetic analysis.

2. Materials and methods

A mixture of toluene, styrene, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK) was chosen as the model VOCs mixture. They are common solvents used in chemical industries. The ratio of the four VOCS in the mixture was based on EPA 2003 emission report from chemical industry [1]. The molar ratio of the four VOCs was 0.448:0.260:0.234:0.058 for toluene:styrene:MEK:MIBK, respectively. The experiment was conducted on two systems for controlling emission of the VOCs mixture. One system consisted of a two-bed adsorption unit followed by a biofilter (integrated system) and the other system was a stand-alone biofilter (control system). The schematic diagram of the two systems was shown in Fig. 1.

2.1. Adsorption unit

The system was designed for operation in a 2-step cycle, i.e., feeding (adsorption) and purging (desorption) within two adsorption beds. The beds were cylindrical and constructed of stainless steel with an external diameter of 2.54 cm and a length of 20.3 cm each. Each bed was packed with 82.5 g BPL carbon 6 × 16 mesh (Calgon Carbon Co., apparent density = 0.85 g/mL). Cyclic operation was generated through an electrically operated 4-way solenoid valve (ASCO 8342G 701, Florham Park, NJ), which was controlled by an electronic timer (Digi 42A-120; GRASSLIN Controls Corp., Mahwah, NJ). The frequency of the cyclic duration was set at 8 h which provided each bed to have 4 h feeding and 4 h purging. A detailed operation is provided elsewhere [21].

2.2. Biofilter unit

Two identical lab scale trickling-bed air biofilters were set up. The biofilter followed the 2-bed adsorption unit is named Biofilter “A”. The other one (Biofilter “B”) was connected directly with the contaminated air stream to act as a control for comparing its performance with the combined system (Adsorption System + Biofilter “A”). Each trickling biofilter 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 (Celite® 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA). The experimental runs were conducted at constant operating temperature of 20 °C. The biofilter was operated in a co-current gas and liquid downward flow mode.

Buffered nutrient solution was supplied at a rate of 2.4 L/day, which provided 17.1 mmol/day $NO_3{}^-$–N feeding, the composition of the nutrient solution was provided in a previous study [2]. *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. During starvation experimental periods, pure air and nutrients solution passed through the biofilters for a period of 2 days per week. No backwashing was employed during starvation experimental periods.

The main air stream was set up at 2.70 L/min and was spilt evenly into two 1.35 L/min sub-air streams, which would result a corresponding empty bed retention time of 2.02 min for biofilters. One stream was introduced to the 2-bed adsorption unit followed by Biofilter “A”. The other stream was introduced directly to Biofilter “B”. Liquid VOC mixture was injected via a syringe pump and vaporized into the main air stream.

2.3. VOC feeding condition

Four square wave changes of inlet concentration shown in Table 1 were considered to simulate transient emission in the chemical industry. A schematic of these square waves is provided in the supplementary material (Fig. S1). In order to provide a square wave change in contaminant concentrations two or three syringe pumps were used.

2.4. Analysis

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). Effluent gas phase sample for CO_2 analysis were also taken by using gas-tight syringes through sampling ports in the biofilter. A GC (HP 5890, Series II, Hewlett-Packard, Palo Alto, CA) equipped with a thermal conductivity detector (TCD) was used for determining the CO_2 concentrations in the effluent gas phase. Liquid phase samples were analyzed for total carbon (TC), inorganic carbon (IC), and volatile suspended solid (VSS) concentration. TC and IC were determined by using a Shimadzu TOC 5050 analyzer (Shimadzu Corp., Tokyo, Japan) according to Standard Methods 5310 [23]. The VSS concentrations in the effluent and backwashing water were determined according to Standard Methods 2540 G [23].

3. Results and discussion

3.1. Cyclic operation of the 2-bed adsorption unit

The behavior of the 2-bed adsorption with cyclic operation under the fourth square wave feeding condition described in Table 1 was investigated for evaluating its buffering capacity. It is worthwhile to note that this square wave is an adverse one and is used to test the behavior of the cyclic adsorption beds under such adverse conditions. The effluent profiles from the 2-bed adsorption unit are shown in Fig. 2.

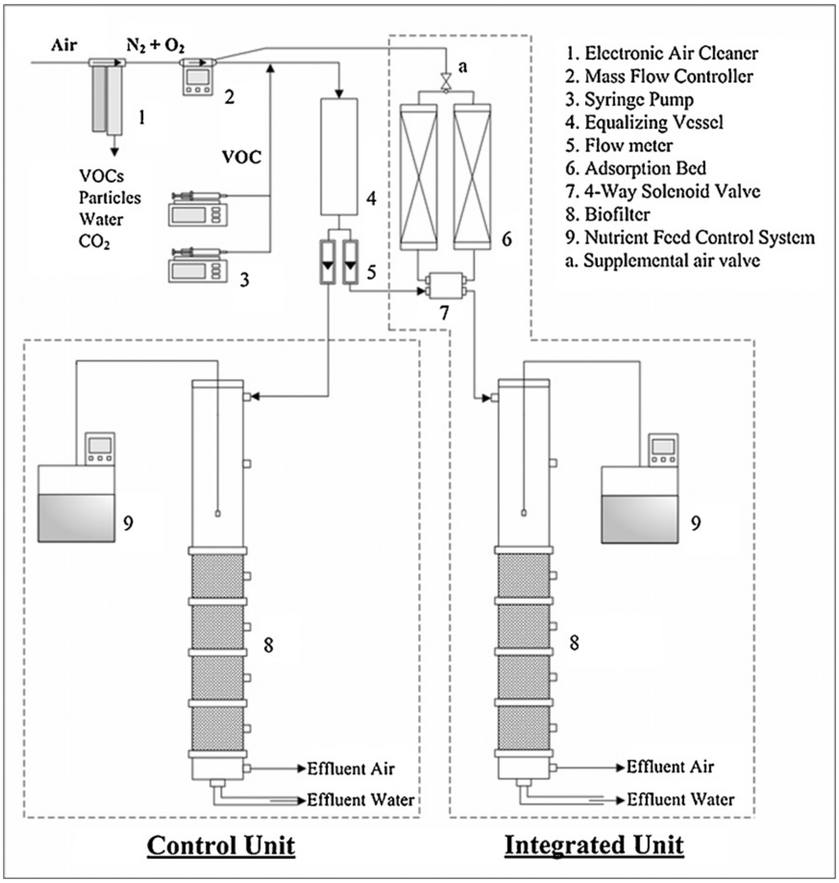

Fig. 1. Schematic diagram of the experimental setup.

It is seen from Fig. 2(a) that the effluent from the 2-bed adsorption unit increased gradually with time and stabilized after 300 h. The total effluent from the 2-bed adsorption unit then fluctuated between 260 and 370 ppmv with an average concentration of 338 ppmv. Such an effluent profile could be of significant impact during initial acclimation of the followed biofilter. Although the effluent exceeded the critical inlet concentration at 300 ppmv [22] in most of the period after stabilization, the magnitude of fluctuation was attenuated significantly as compared with the fluctuation in the feeding condition. A more stable removal performance can be expected from the followed biofilter as compared to a standalone biofilter under such feeding conditions.

Table 1
Square wave inlet VOCs feeding conditions.

	First	Second	Third	Fourth	
Average concentration (ppmv)	302.5	300	350	450	
Total average loading rate (g/(m^3 h))	34.3	34.0	39.6	50.9	
Average toluene loading rate (g/(m^3 h))	15.5	15.4	17.9	23.0	
Average styrene loading rate (g/(m^3 h))	10.2	10.1	11.8	15.1	
Average MEK loading rate (g/(m^3 h))	6.4	6.3	7.4	9.5	
Average MIBK loading rate (g/(m^3 h))	2.2	2.2	2.5	3.3	
Frequency of square wave per hour	1	1	2	2	
Inlet concentration					
Peak concentration (ppmv)	700	500	500	700	500
Duration (min/h)	7	12	24[a]	15	15
Total loading rate (g/(m^3 h))	79.5	56.5	56.5	79.5	56.5
Toluene loading rate (g/(m^3 h))	35.8	25.6	25.6	35.8	25.6
Styrene loading rate (g/(m^3 h))	23.7	16.8	16.8	23.7	16.8
MEK loading rate (g/(m^3 h))	14.8	10.5	10.5	14.8	10.5
MIBK loading rate (g/(m^3 h))	5.2	3.6	3.6	5.2	3.6
Base concentration (ppmv)	250	250	250	300	
Total loading rate (g/(m^3 h))	28.3	28.3	28.3	34.0	
Toluene loading rate (g/(m^3 h))	12.8	12.8	12.8	15.4	
Styrene loading rate (g/(m^3 h))	8.4	8.4	8.4	10.1	
MEK loading rate (g/(m^3 h))	5.3	5.3	5.3	6.3	
MIBK loading rate (g/(m^3 h))	1.8	1.8	1.8	2.2	

[a] The duration of 500 ppmv concentration was split into two durations of 12 min each repeated after 18 min duration of the base concentration (see Fig. S1 in the supplementary material).

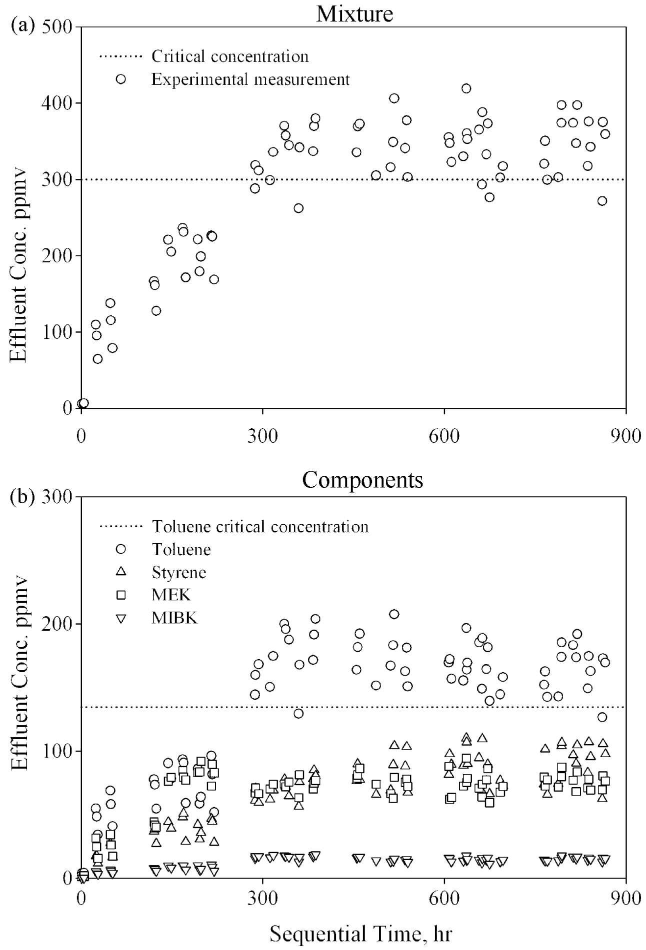

Fig. 2. (a) Experimental measurement of the effluent VOCs mixture concentration and (b) experimental measurement of the effluent components in the mixture with cyclic operation of the adsorption beds.

Effluent profiles for the components in the mixture from the adsorption unit are shown in Fig. 2(b). After stabilization, the effluent concentration of toluene fluctuated between 150 and 200 ppmv with an average concentration of 167 ppmv, styrene fluctuated between 60 and 120 ppmv with an average concentration of 82 ppmv, MEK fluctuated between 60 and 100 ppmv with an average concentration of 74 ppmv, and MIBK fluctuated between 5 and 20 ppmv with an average concentration of 15 ppmv. The effluent molar fraction with sequential time for the four components of the mixture is shown in Fig. 3. It can be seen from Fig. 3 that the initial effluent of toluene and styrene had a low percentage in the effluent mixture and then increased and stabilized at 0.49 and 0.24, respectively. Furthermore, styrene stabilized sooner than toluene. MEK had high molar fraction initially and then decreased and stabilized at around 0.22. MIBK maintained stable fraction in the effluent mixture at around 0.04. Compared to the molar fraction in the feeding condition (0.448, 0.260, 0.234, and 0.058 for toluene, styrene, MEK, and MIBK, respectively), it can be deduced that competitive adsorption occurred in the 2-bed adsorption unit. The competitive adsorption effects can be contributed to adsorbates differences in physicochemical properties [19,24]. This finding is consistent with the findings by Li and Moe [15] where they found that the degree of load equalization achieved in a single adsorber bed varied among the different constituents of the gas mixture.

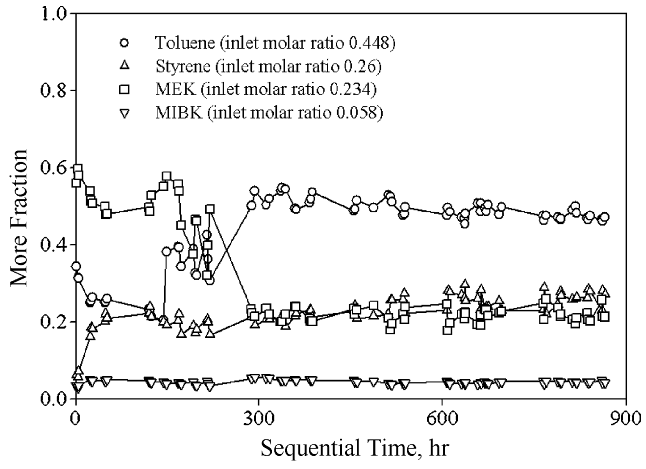

Fig. 3. Mole-fraction of the different mixture components in the effluent of the 2-bed cyclic adsorption unit.

3.2. Comparison of biofilter performance

The performance of Biofilter "A" and Biofilter "B" for the first square wave of inlet concentration is shown in Fig. 4. The inlet VOC mixture concentration to Biofilter "A" was the effluent from the 2-bed cyclic adsorption unit. After the effluent concentration from the cyclic adsorption unit stabilized, the inlet concentration to Biofilter "A" fluctuated from 180 to 280 ppmv. Since the variations of the inlet concentration to Biofilter "A" were close to the critical concentration (300 ppmv) [22], Biofilter "A" consistently maintained a removal level above 99% after a very short initial acclimation period as shown in Fig. 4(a). Biofilter "A" showed a very short period of initial acclimation to toluene and styrene (data not shown), and then maintained consistent over 99% removal efficiency for both components. For the remaining two components MEK and MIBK acclimation was not needed and the biofilter maintained a consistent removal of 99% for these two components (data not shown). On the other hand, the performance of Biofilter "B" fluctuated from 85% to 99% removal level as shown in Fig. 4(b). Biofilter "B" showed periodical fluctuation in performance corresponding to the backwashing cycles which were conducted once per week. After backwashing, the biofilter removal efficiency increased, then gradually decreased with time and sometimes provided removal efficiency as low as 85% just prior to next backwashing operation. Biofilter "B" required apparent initial acclimation to toluene and

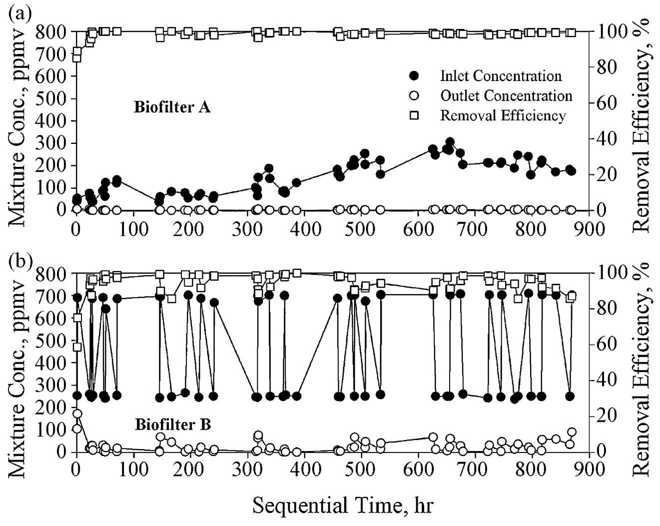

Fig. 4. Biofilter performance under the first square wave feeding condition. (a) Biofilter "A"; (b) Biofilter "B".

styrene in the mixture (data not shown). The over all performance for the mixture was strongly dependent on the performance of toluene in the mixture. The biofilter maintained a consistent over 99% styrene removal efficiency after initial acclimation. It did not require an acclimation period for MEK and MIBK and the biofilter maintained a consistent over 99% removal efficiency for these two components.

The performance for Biofilter “A” and Biofilter “B” for the second square wave feeding condition was different from that for the first square wave (see Fig. S2 in the supplementary material). After a short period of stabilization period, the inlet concentration for Biofilter “A” was about 200 ± 50 ppmv. At this concentration level, Biofilter “A” maintained consistent 99% removal efficiency without apparent acclimation period because the inlet concentration did not exceed the critical concentration of 300 ppmv. Meanwhile, the four components in the mixture maintained consistent 99% removal efficiency (data not shown). On the other hand, the control biofilter (Biofilter “B”) could not maintain consistent 99% removal efficiency although the average inlet concentration was at the critical concentration of 300 ppmv. The removal efficiency fluctuated from 90% to 99% due to the high inlet concentration fluctuations between 250 and 500 ppmv. It was further noticed that the overall performance of the biofilter was controlled by toluene. The removal efficiency for toluene in the mixture fluctuated between 80% and 99% after an initial acclimation period (data not shown). The removals of other components in the mixture were maintained consistently above 99% removal efficiency without apparent acclimation period.

On comparing the performance of Biofilter “B” under the second square wave feeding condition to the first square wave it is seen that the second square wave provided better performance although the average inlet concentration was similar for the two feeding conditions. The first square wave had higher peak concentration with shorter duration as compared with the second square wave feeding condition. This could indicate that the magnitude in inlet concentration fluctuation had more impact on the biofilter performance than its duration under similar overall loading rates.

For the third and fourth square wave feeding conditions, more fluctuations were employed. After initial stabilization period for the effluent from the 2-bed cyclic adsorption unit, the inlet concentration for Biofilter “A” fluctuated between 200 and 330 ppmv for the third square wave (see Fig. S3 in the supplementary material). The removal efficiency was maintained over 97%, but the 99% removal level could not be maintained due to peak concentrations over the critical concentration of 300 ppmv to the biofilter from time to time. Toluene removal efficiency fluctuated between 95% and 99% (data not shown). The removals of the other three components in the mixture were maintained consistently over 99%. It is thus seen that the biofilter overall performance was controlled by toluene performance in the mixture. On the other hand, the removal efficiency for Biofilter “B” fluctuated from 76% to 95%. Toluene removal efficiency in the mixture fluctuated between 50% and 93% (data not shown). Styrene removal efficiency could be maintained at 99% after backwashing; however, it then decreased gradually to around 85% just prior to next backwashing. This biofilter maintained consistent over 99% removal efficiency for MEK and MIBK in the mixture. For Biofilter “B” the overall performance was controlled by the performance of toluene and styrene in the mixture.

For the fourth square wave feeding conditions, after an initial stabilization period, the inlet concentration for Biofilter “A” fluctuated between 300 and 400 ppmv (see Fig. 5(a)). The removal efficiency fluctuated from 88% to 97%. Toluene removal in the mixture fluctuated between 75% and 99% (data not shown). Styrene removal reached 99% after backwashing and then decreased gradually to 95% just prior to next backwashing. Biofilter “A” maintained consistently over 99% removal efficiency for MEK and MIBK in the mixture. In case of the control biofilter (Biofilter “B”), it is seen that the removal efficiency for the mixture fluctuated from 60% to 85% (Fig. 5(c)). Toluene removal efficiency fluctuated between 40% and 75%. Styrene removal efficiency fluctuated between 78% and 99%. Biofilter “B” maintained consistently over 99% removal efficiency for MEK and MIBK in the mixture.

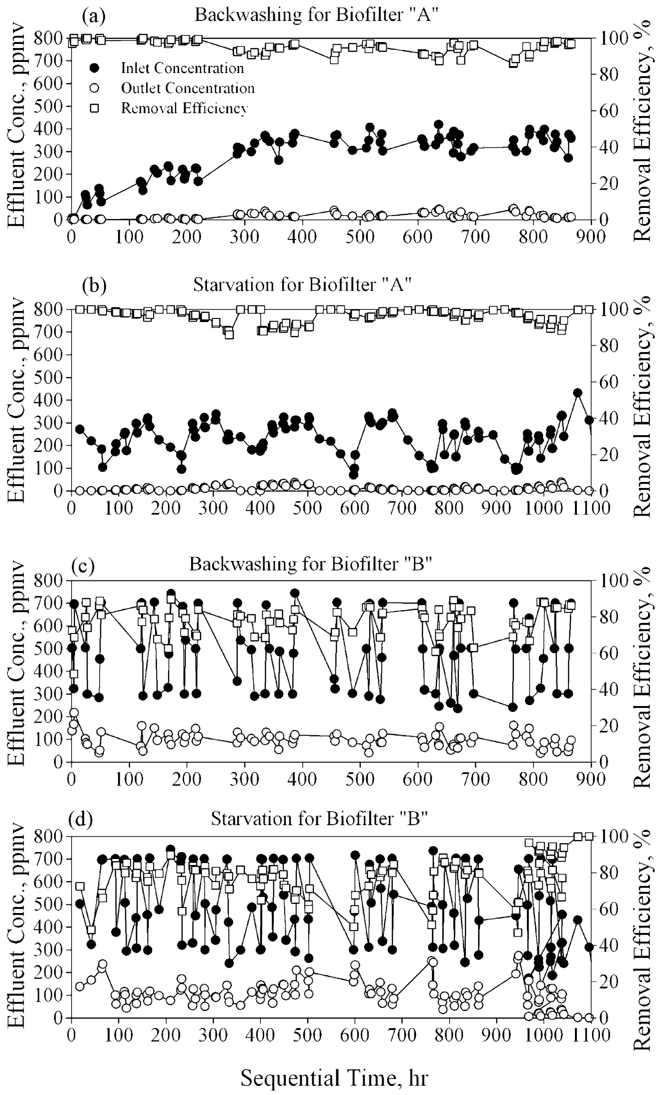

Fig. 5. Performance comparison between backwashing and starvation operation for Biofilters “A” and “B” under the fourth square wave feeding condition. (a) Backwashing for Biofilter “A”; (b) starvation for Biofilter “A”; (c) backwashing for Biofilter “B”; (d) starvation for Biofilter “B”.

The performances of Biofilters “A” and “B” under the fourth square wave feeding condition showed lower removal capacity as compared to the previous square waves studied due to the increase of frequency and magnitude of the square wave. However, the inlet concentration profiles for Biofilter “A” indicated that the proceeded cyclic 2-bed adsorption/desorption unit succeeded in attenuating the fluctuation as compared with the inlet concentration profiles for Biofilter “B”. This led to significant improvement of the performance of Biofilter “A” as compared to Biofilter “B”.

A brief summary of the performance is provided in Fig. 6. Fig. 6 provides a box plot for the effluent concentrations from Biofilters “A” and “B” under the four square wave feeding conditions. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. The error bars above and below the box indicate the 90th and 10th percentiles.

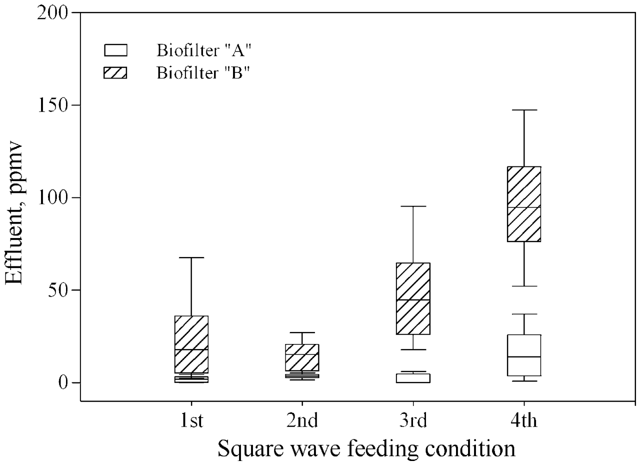

Fig. 6. Performance comparison between the integrated system (2-bed adsorption + Biofilter "A") and the control system (Biofilter "B").

For the first two square waves, it is seen from Fig. 6 that the effluent concentration from the integrated system was varying within a narrow range almost approaching zero while the control system (Biofilter "B") provided wide variations that sometimes exceeded 50 ppmv for the first square wave. The effluent concentration from the integrated system for the third square wave showed significant improvement over the control system. For the fourth square wave which was more aggressive in fluctuations as compared to the previous three square waves, the effluent from the control system (Biofilter "B") was exceedingly high with the 75th percentile above 100 ppmv while that for the integrated system was less than 40 ppmv. The results clearly indicate that the integrated system provided superior performance as compared to the control system.

3.3. *Starvation effect on the integrated system and control system*

After the fourth cycle of backwashing during the fourth square wave feeding condition, the syringe pumps feeding the VOCs to the system were stopped for a period of 2 days per week in order to study the impact of starvation on both biofilters. In case of Biofilter "A" the 2-bed cyclic adsorption system acted as a feeding source to the biofilter by desorbing the adsorbed VOCs during the off periods of the syringe pumps. Fig. 5 compares the performance of Biofilters "A" and "B" under the two operating strategies, i.e., backwashing which was discussed previously and starvation. The results shown in Fig. 5(b) indicate that the variations in the influent which sometimes dropped to 100 ppmv were due to desorption of the VOCs from the 2-bed cyclic adsorption unit during the starvation period. Meanwhile, the influent concentration to Biofilter "A" during the days of operation of the syringe pumps decreased to around 300 ppmv as compared to around 350 ppmv for backwashing operation. The decreased overall influent to the biofilter resulted in providing consistent over 99% removal efficiency initially. The biofilter later showed drop in removal efficiency due to excess accumulation of biomass which could induce channeling of air within the biofilter. Therefore, after 600 h, the biofilter was backwashed to remove the excess biomass, and the biofilter regained its consistent 99% removal efficiency. The results in Fig. 5(b) indicate that the cyclic 2-bed adsorption unit successfully acted as feeding source to the followed biofilter during starvation operating periods and no apparent re-acclimation periods were required for recovering the original performance. The desorption of the VOCs by the 2-bed adsorption system during starvation periods reduced the accumulated VOCs in the adsorption beds and helped in maintaining the buffer capacity of the 2-bed adsorption unit for a longer period. Meanwhile, periodic backwashing was necessary to maintain consistent high level performance for the biofilter under starvation operating conditions because the loading rate was around the critical loading capacity for the biofilter.

Fig. 5(c) and (d) shows a comparison between the two strategies, i.e., backwashing and starvation for the control biofilter (Biofilter "B"). It is clearly seen that the starvation strategy under the aggressive fourth square wave of inlet concentration provided poor performance. The performance sometimes dropped to below 50% and the over all performance was worse than the backwashing (Fig. 5(c)). This behavior was expected because starvation could not be used as a means of biomass control for high loading rates exceeding the critical loading rate [22].

It is worthwhile to note that if the cyclic adsorption bed is exhausted after a long period of use, it can be used as a feeding source to the biofilter in order to regenerate its original capacity.

3.4. *Carbon mass balance*

The cumulative CO_2-equivalent of VOCs consumed during all experimental runs was compared to the cumulative CO_2-equivalent produced within Biofilter "A" and Biofilter "B". The inlet (or outlet) cumulative CO_2-equivalent was estimated as the total cumulative CO_2-equivalent in the influent (or effluent) aqueous and gaseous streams. There is very good closure between the two cumulative values for both biofilters under the first three square waves inlet concentration conditions (data shown in supplementary material Fig. S4).

The CO_2-equivalent closure for the fourth square wave is shown in Fig. 7. It is seen from Fig. 7(a) that there is very good closure between the two cumulative values (inlet and outlet) for the biofilter for the backwashing strategy. For Biofilter "A", the outlet cumulative CO_2-equivalent was about 98.1% of the inlet cumulative CO_2-equivalent at the end of experiment. For Biofilter "B", the outlet cumulative CO_2-equivalent was about 97.4% of the inlet cumulative CO_2-equivalent at the end of experiment. It is worthwhile to note that the inlet cumulative CO_2-equivalent for Biofilter "A" was 63.9% of the inlet cumulative CO_2-equivalent for Biofilter "B", which indicated that 36.1% of the VOCs in the mixture were adsorbed by the adsorbent in the 2-bed cyclic adsorption unit. In case of the starvation strategy, it is seen from Fig. 7(b) that there are obvious deviations between the two cumulative values. These deviations could be due to unwashed biomass within the biofilter

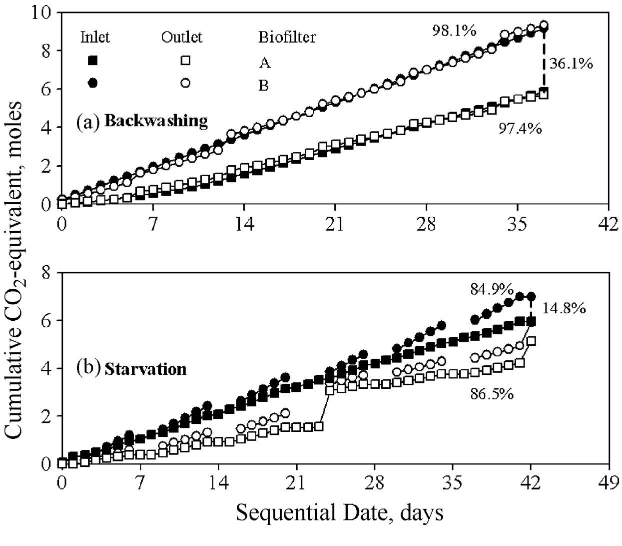

Fig. 7. CO_2-equivalent closure for Biofilter "A" and Biofilter "B" with time for the fourth square wave feeding condition. (a) Backwashing; (b) starvation.

which is not accounted for. The inlet cumulative CO_2-equivalent for Biofilter "A" was 85.2% of the inlet cumulative CO_2-equivalent for Biofilter "B", which indicated that 14.8% of the VOCs in the mixture were adsorbed by the adsorbent in the 2-bed adsorption unit. Compared with the operation under backwashing strategy, most of the adsorbed VOCs in the 2-bed adsorption unit were released during starvation operation indicating that the cyclic 2-bed adsorption system successfully functioned as feeding source to Biofilter "A" during starvation periods and in turn delayed the saturation time to the 2-bed adsorption unit significantly.

3.5. Removal kinetic analysis

One day following backwashing, gaseous samples were taken along the media depth of the biofilter to assess removal kinetics for VOC removal during low and high peak inlet concentration periods. 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 to 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. 8 represents plots of toluene and styrene first order removal rate constants under the four square wave feeding conditions. The removal rates along the biofilter media depth for MEK and MIBK could not be determined because of complete removal of MEK and MIBK within the upper 3/8 media depth. The obtained removal rates for toluene and styrene in Fig. 8 showed that there were significant difference between the low and the high peak inlet concentration in removal rates for Biofilter "B" (control unit), and the removal rates at low peak inlet concentration were apparently higher that those at high peak inlet concentration. However, the removal rates between low and high peak inlet concentration were very close for the integrated system (2-bed cyclic adsorption unit + Biofilter "A"), which could be contributed to the effective dampening of the inlet concentration fluctuation by the cyclic 2-bed adsorption unit. Furthermore, both biofilters showed higher removal rates for styrene than toluene, which was consistent to single solute results in our previous studies [25,26].

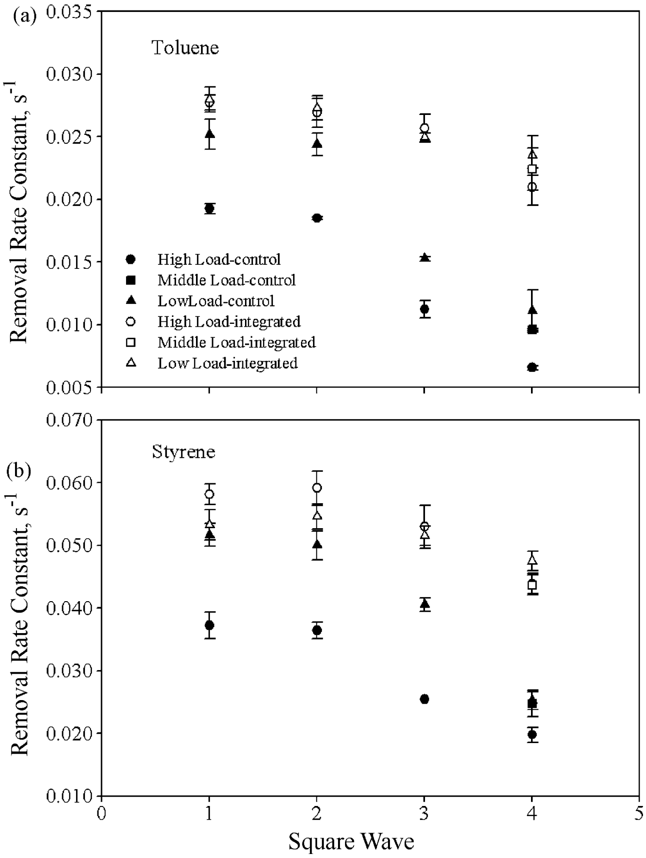

Fig. 8. Toluene and styrene removal rates under backwashing operating conditions. (a) Toluene; (b) styrene.

4. Conclusions

This study evaluated the buffering capacity of a 2-bed cyclic adsorption unit. The 2-bed cyclic adsorption unit succeeded in providing low effluent that reduced the initial acclimation time of a followed biofilter and also attenuated significantly the fluctuation in inlet concentration after stabilization. This study further investigated the performance of a trickling-bed air biofilter integrated with a 2-bed cyclic adsorption/desorption unit for the removal of a mixture of VOCs under different square wave feeding conditions. The behavior of a control experiment in performance and removal kinetics along the biofilter depth was compared with the integrated system. The integrated system was validated to maintain long-term consistent high level removal efficiency of a mixture of VOCs. The pseudo first order removal rate constants varied with the fluctuation of feeding conditions for the control system, however, no apparent difference for the integrated system was seen due to the effective dampening of the 2-bed cyclic adsorption unit to the feed inlet concentration. The integrated system can provide a satisfied engineering way to solve the fluctuations in VOC emission conditions which could challenge the application of the biofiltration technology in VOC emission control.

Acknowledgements

The authors thank the financial support from National Science Foundation under award # BES 0229135. The finding and conclusions expressed in this publication are solely those of the authors and do not necessary reflect the views of the foundation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2009.02.002.

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