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Ethylene removal using biotrickling filters: Part I. Experimental description

Sang-Hun Lee [a,*], Congna Li [a], Albert J. Heber [a], Cheng Zheng [b]

[a] *Department of Agricultural and Biological Engineering, Purdue University, 225 South Street, West Lafayette, IN 47907-2093, USA*
[b] *Department of Statistics, Purdue University, 250 North University Street, West Lafayette, IN 47907-2066, USA*

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ABSTRACT

The control of liquid flow is one of the most significant factors that affect operation of biotrickling filters. This study evaluated removal of ethylene (C_2H_4) using biotrickling filters at various liquid recirculation flow rates. Perlite and glass beads were utilized as media in eight and two reactors, respectively. Trickle liquid recirculation flow rates ranging from 2.7 to 26 L h^{-1} (velocity of 0.4–3.7 m h^{-1}) were used. Two perlite reactors were operated with the liquid being recirculated intermittently for 10 min every hour at a recirculation flow velocity of 13 L h^{-1} (velocity of 1.9 m h^{-1}). Inlet gas contained about 30 mg m^{-3} of C_2H_4 and 0–40 mg m^{-3} of ammonia (NH_3).

The results showed that C_2H_4 removal efficiencies increased as time elapsed, but the increasing rate of C_2H_4 removal was different based on the reactor types. One of the two perlite biotrickling filters with low liquid recirculation flow exibited a high C_2H_4 removal up to 90%, but other biotrickling filters reached only about 40–70% of C_2H_4 removal efficiency, due to either a relatively high mass transfer limitation or poor distribution of nutrients. This study denotes that a trickle liquid flow over 0.8 m h^{-1} (5.4 L h^{-1}) had a significant detrimental effect on ethylene removal due to high mass transfer limitation that suppresses microbial growth for ethylene degradation. Therefore, the perlite biotrickling filters with flow rates as low as 0.4 m h^{-1} (2.7 L h^{-1}) can gave the best performance in high ethylene removal.

1. Introduction

Biofiltration utilizes microorganisms attached to surfaces inside the media bed to degrade gas-phase contaminants. The contaminants consumed by microorganisms are ultimately transformed into non-toxic chemicals including CO_2, H_2O, and microbial cellular materials. Microbial degradation requires low energy consumption, and has therefore been considered as a potential air treatment technology [1].

Biofiltration has been classified into three types: biofilters, biotrickling filters, and bioscrubbers [1]. Among these types, biotrickling filters are advantageous for continuous nutrient supply to the media and removal of moderately biodegradable contaminants [1].

The aqueous solution, referred to as liquid in this study, containing water and nutrient minerals, is continuously recirculated through the media in the operation of a biotrickling filter. The chemicals in the gas are transported via convection along the vertical direction of the media bed inside the reactor. The contaminants in the gas phase are dissolved into the liquid phase and then diffuse into the biofilm phase to be degraded.

C_2H_4, which is the target compound in this study, has been considered as one of the major gaseous contaminants generated from plants or petrochemical products [2–5]. This compound may not be easily removed by biotrickling filtration, because the low solubility of C_2H_4 hampers its mass transfer from the gas to liquid phases [1,3]. According to a previous study with C_2H_4 biofilter, an EBRT (Empty Bed Residence Time) of 9 min was required to reduce 117 ppm of inlet C_2H_4 to less than 0.04 ppm by C_2H_4-oxidizing microorganisms [3]. The retention time was much longer than those of biofilters treating hydrophilic contaminants.

On the other hand, another type of oxidation of C_2H_4 may be possible if coupled with oxidation of NH_3 into nitrite. Hommes et al. [6] observed that NH_3 monooxygenase enzyme in *Nitrosomonas europaea* can oxidize several hydrocarbons including C_2H_4. An C_2H_4 biofilter applying such co-oxidation was reported by De heyder et al. [7]. Less than 1000 ppm of C_2H_4 was significantly reduced, up to 40% removal efficiency, using a GAC (Granular Activated Carbon)-based biofilter with an EBRT of 60–90 s. Tambwekar et al. [9] reported that about 99% C_2H_4 removal was accomplished in perlite-based biofilters with an inlet C_2H_4concentration of 10 ppm when EBRT was 2 min. NH_3 was loaded with C_2H_4 for possible co-oxidation.

The microorganisms for ethylene biofiltration were also investigated. Microorganisms known to be involved in C_2H_4 degradation are *Mycobacterium*, *Pseudomonas* strains and *N. europaea*

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* Corresponding author. Tel.: +1 765 490 4242; fax: +1 765 496 1115.
E-mail address: lee323@purdue.edu (S.-H. Lee).

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[4,6,7,9–11]. Miller and Allen [8] reported that compounds that are insoluble in water can efficiently be eliminated by biofiltration, when biologically-mediated transformation oxidizes the compounds into soluble forms.

However, no previous study evaluated the effect of the liquid (or water) amount on C_2H_4 removal, although the liquid content in media is known to be one of the most important factors in biofiltration [1,12–15]. Because of the low solubility, C_2H_4 removal should be greatly affected by the presence of the liquid amount in biofiltration. van Lith et al. and Morales et al. also stated that lots of biofilter malfunction was caused by inadequate management of the water content in the filter material [15,16].

Excessive water potentially reduces media porosity and increases mass transfer limitations that prevents the mass transfer of hydrophobic contaminants, oxygen and CO_2 across the water film around microorganisms. The mass transfer limitation of oxygen may cause anaerobic zones in the filter beds leading to severe odor generation. On the other hand, an insufficient water amount reduce aqueous chemical reactions and microbial activity, which has the most detrimental effect on biofilter performance [15,17,18].

Some previous studies show that high levels of moisture condition are generally desirable for biofiltration. Lee et al. [19] observed that the removal efficiency of a peat biofilter at 57% moisture content wet basis decreased to almost zero when the moisture content decreased to 37%. In a biofilter with organic media, the removal efficiency of α-pinene was much less with partially wetted media than fully wetted [17,20]. However, for iso-pentane degradation in compost, while an irreversible decline in performance was observed at a moisture content of compost lower than the optimal moisture content, there was a drop in removal efficiency for moisture contents above optimal values [21]. A similar response to the moisture levels is possible for other insoluble compounds.

It is not easy to directly evaluate the effects of the liquid or water content of media in biofiltration reactors in operation. Therefore, this study evaluates C_2H_4 removal as influenced by controlling liquid recirculation, through which moisture content can be controlled indirectly. The effects of inlet concentrations of C_2H_4, media types, and media bed depth on C_2H_4 removal were observed as well.

2. Materials and methods

2.1. Bioreactors

A schematic diagram of a biotrickling filter used for the experiment is shown in Fig. 1. The reactor was 0.81-m high and had an internal diameter of 10 cm. The column of the reactor was made of PVC (Polyvinyl Chloride) plastic (Ryan Herco, Naperville, IL), and was sealed at each end with PVC flanges (Ryan Herco, Naperville, IL) by bolted gaskets [22]. The maximum packed bed height was 56 cm. A liquid sprinkler was located at the top interior of the reactor. Each sprinkler was made of a plastic jar (Jars Nalgene style 2118 size 250 mL, Sigma–Aldrich, USA), in which many small holes. Liquid in a peristaltic pump moved from the reservoir to the sprinkler nozzle. Then, the liquid stored in the sprinkler trickled downward via gravitational force without any external pressure. The spraying was monitored and sometimes adjusted to provide homogeneous media wetting.

A perforated plate with 2-mm holes was located near the bottom of the column to support the media bed and drain the liquid. The liquid was drained through the openings collected in a 1.8-L external glass reservoir and recirculated into the reactor by a peristaltic pump (Model no. 77521-50 Masterflex, Cole-Parmer, Barrington, IL). Deionized water was daily added to the external liquid reservoir to compensate for water loss due to evaporation.

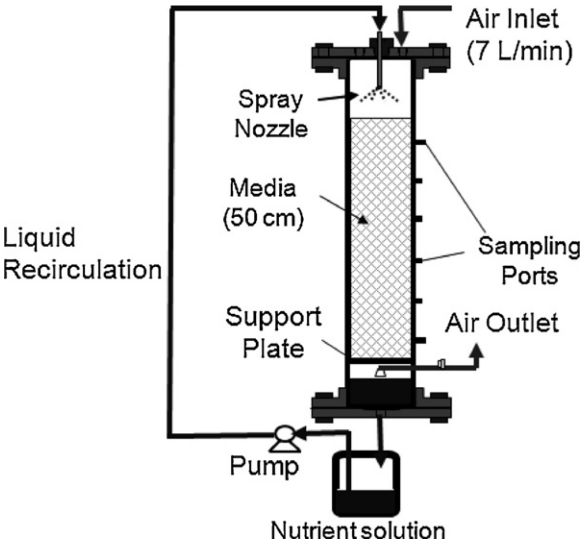

Fig. 1. Schematic diagram of the biotrickling filter.

The gas inlet and outlet ports were located at the top and the bottom of the media bed, respectively. Six gas sampling ports were evenly distributed along the height of the columns to allow periodic gas sampling at intermediate heights. The reactor room temperature was maintained at 20 °C.

The primary packing medium used in six biotrickling filters was 3.5-mm perlite (Ryolex Industry Perlites, Silbrico Co., Hodgkins, IL). The porosity, surface area, and water holding capacity of perlite is 90%, $3.5\,m^2\,g^{-1}$, and $6\,L\,kg^{-1}$, respectively [23]. Glass beads (McMaster Carr Co., Elmhurst, IL) with diameters of 6 mm were used in the other two biotrickling filters. The use of glass beads is not a desirable choice with respect to high contaminant removal by biofiltration, it is often helpful for developing theoretical models. The bulk porosity and the surface area of the glass beads were assumed to be 35–50% and $1000\,m^2\,m^{-3}$ in this study ($\approx$6/diameter). The measured water holding capacity of the glass beads was $26\,g\,m^{-3}$, which was obtained using the weight difference between dried media and fully wetted media.

2.2. Injection of C_2H_4 and NH_3

An air compressor (5.6 KW, Ingersol-Rand, Indianapolis, IN) provided air after purification by oil and carbon filters. C_2H_4 and NH_3 were injected from pressurized gas cylinders containing each gas. The NH_3 gas cylinder contained 5% NH_3 in N_2 (Praxair, Los Angeles, CA), and the C_2H_4 cylinder had 99.5% C_2H_4 (Scott Specialty Gases, Plumsteadville, PA). The gases from the cylinders were mixed with the compressed air to produce an ersatz gas stream, before entering the mixing manifold. Flow rates were adjusted by 3-mm double pattern needle valves (SS-410-FP-D, Swagelok Co., Solon, OH) to provide the target inlet contaminant concentrations. Water vapor generated by a steam generator (Model LB-10, Electro-Steam Generator Corp., Alexandria, VA) was injected into the gas mixing manifold in the reactor room to humidify the contaminated gas stream. An average relative humidity was controlled from 50% to 65% at a reactor room temperature of 20 °C. The ersatz cabin gas stream flowed into a stainless steel gas supply manifold in the reactor room, where the mixed stream flow was controlled and evenly distributed to each bioreactor inlet. The target flow rate for each reactor was $6.9–7.5\,L\,min^{-1}$ with 30 s of EBRT under steady loading. A diagram of the entire experimental setup for the contaminant injection, gas sampling, and analysis is depicted in Fig. 2.

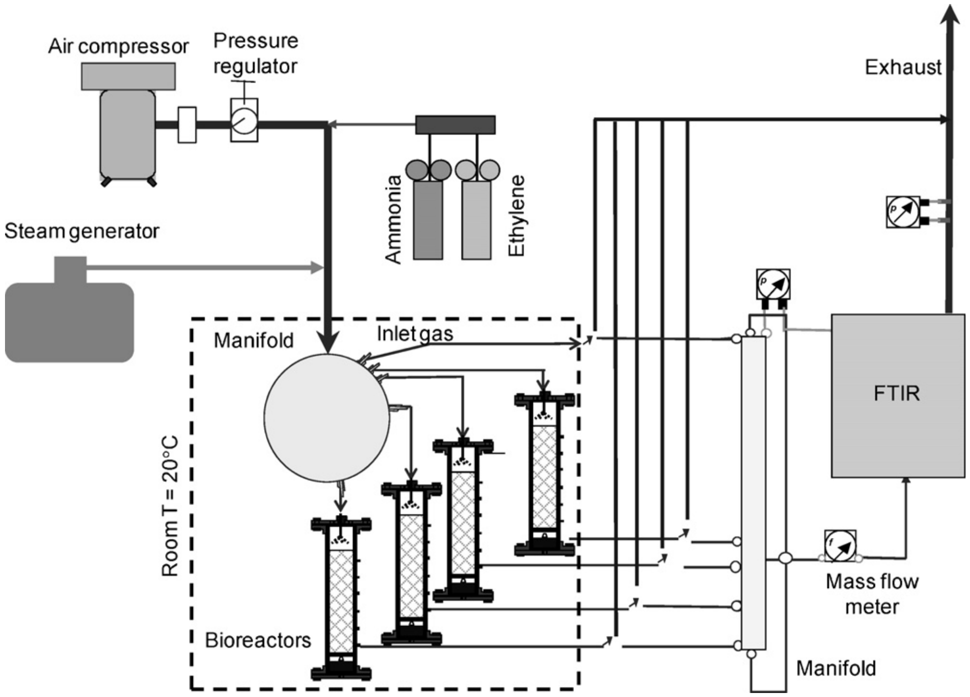

Fig. 2. Schematic diagram of the experimental setup.

2.3. Inoculation and nutrient solution

Before the test began, each bioreactor was seeded with activated sludge from a wastewater treatment plant (West Lafayette, IN). The suspended sludge was settled for 2 h to obtain concentrated sludge after the supernatant was discarded. The concentrated sludge was mixed with fresh nutrients in 1:9 ratios, and recirculation of the liquid started with the mixed suspension in each reactor for 10 h prior to starting the normal operation of the reactors.

The fresh nutrient solution consisted of the following chemical compounds [22,24]: $NaNO_3$ ($2\,g\,L^{-1}$), KH_2PO_4 ($0.5\,g\,L^{-1}$), Na_2HPO_4 ($0.2\,g\,L^{-1}$), $MgSO_4$ ($20\,mg\,L^{-1}$), $CaCl_2{\cdot}2H_2O$ ($3.0\,mg\,L^{-1}$), $FeSO_4{\cdot}7H_2O$ ($0.5\,mg\,L^{-1}$), $ZnSO_4{\cdot}H_2O$ ($0.4\,mg\,L^{-1}$), $MnSO_4{\cdot}H_2O$ ($0.1\,mg\,L^{-1}$), $CuSO_4{\cdot}5H_2O$ ($0.01\,mg\,L^{-1}$), $CoCl_2{\cdot}6H_2O$ ($0.007\,mg\,L^{-1}$), H_3BO_3 ($0.57\,mg\,L^{-1}$), and $Na_2MoO_7{\cdot}2H_2O$ ($0.005\,mg\,L^{-1}$).

After day 76 of the experiment onward, the nutrient recipe was changed to include $0.75\,mg\,L^{-1}$ of KH_2PO_4 and $11\,g\,L^{-1}$ of Na_2HPO_4 to test enhancement of the pH buffering capacity and $1\,g\,L^{-1}$ of $NaHCO_3$ as the supplemental inorganic carbon source to enhance oxidation of NH_3. The liquid in each storage reservoir was replaced with new fresh nutrient solution every 7 days. The pH of the liquid was analyzed daily using a pH meter (Oaklon Model 5/6, Oaklon Instruments, Vernon Hills, IL) and adjusted to a value between 7 and 8 using 8 M NaOH and concentrated phosphoric acid. The detection limit of the pH meter was approximately 0.01. The air pressure drop in each reactor was measured between the top and a selected depth of the media (300 Durablock, Dwyer Instrument Inc., Michigan City, IN). The detection limit for the pressure drop measurement was assumed to be 0.1 mm H_2O. The measurements were conducted approximately monthly.

2.4. Sampling and analytical methods

The inlet and outlet gas streams from the bioreactors were collected using an automatic multi-point gas sampling system. Three-way Teflon-lined solenoid valves (Part No. 98300-42, Neptune Research, West Caldwell, NJ) were utilized to sequentially select the outlet from a reactor or the inlet manifold. The sampling sequence was controlled by Data Acquisition and Control hardware (FieldPoint, National Instruments Co., Austin, TX) and software (Labview 7.0, National Instruments Co., Austin, TX).

The gas concentrations were measured with an FTIR spectrometer (Nexus 670, Thermo Electron Corporation, Palatine, IL). The spectrometer software (OMNIC QuantPad, Thermo Nicolet Instrument Corporation, Madison, WI) automatically calculated the concentrations of the gases, based on spectra signals. The detection limit and the resolution of the FTIR spectrometer were $0.005\,mg\,m^{-3}$ and $0.5\,cm^{-1}$, respectively. During the FTIR measurement of inlet and outlet gas concentrations, the sampling period was typically 10 min. Since residual gas remaining from previous sampling may interfere with measurement of the current sample, the concentrations of the last 3 min of a sampling period were chosen to represent reactor concentration for the current sampling cycle. The daily mean gas concentration for a given reactor was obtained by averaging the sample collected for the day.

2.5. Operation methods

The reactor treatment sets are described in Table 1. Each set consisted of two reactors with replication, with 30 s of EBRT. All of the biotrickling filters were operated with continuous liquid recirculation rates. On day 92, the recirculation flow rate for each of the bioreactors was reduced by 50%, which was the beginning point of the C_2H_4 removal. The liquid recirculation rate for BTF-H was increased during days 131–142 to observe the effects of the variation of the liquid recirculation rates on removal efficiency. From days 176 to 181, the liquid flows in BTF-L1, BTF-M1, BTF-H1, BF1, and BTF-GB1 were terminated to compare the performance of each reactors with its corresponding duplicated counterpart.

All of the bioreactors were operated at normal loading conditions over the entire experiment. Under normal loading conditions, the reactors received constant amounts of both NH_3 and C_2H_4. The concentrations of inlet air from the manifold and outlet concentrations of air flowing from the bioreactor outlets were monitored to calculate daily contaminant removal efficiencies. Inlet NH_3 concen-

Table 1
Design configurations of the reactors.

Treatment sets	Reactors	Media types	Liquid flow rates
BTF-L	BTF-L1 BTF-L2	Perlite	Low[a]
BTF-M	BTF-M1 BTF-M2	Perlite	Middle[a]
BTF-H	BTF-H1 BTF-H2	Perlite	High[a]
BF	BF1 BF2	Perlite	Intermittent[a,b]
BTF-GB	BTF-GB1 BTF-GB2	Glass beads	Low[a]

[a] Detailed information is shown in Table 2.
[b] Nutrients will be recirculated intermittently in these bioreactors for 10 min per hour.

trations were generally maintained at 20–30 $\mathrm{mg\,m^{-3}}$, but increased to about 40 $\mathrm{mg\,m^{-3}}$ during days 142–153, and were reduced to zero after day 162. The inlet C_2H_4 concentrations under normal loading ranged from 20 to 35 $\mathrm{mg\,m^{-3}}$ (typically 30 $\mathrm{mg\,m^{-3}}$).

The entire experimental period was divided into seven phases, according to steady-state inlet levels or liquid recirculation rates. The second and third phases underwent significant changes of liquid recirculation rates, pH adjustment, and nutrient recipes. The experimental conditions are summarized in Table 2. Short-term variations of liquid recirculation rates in the BTF-H and BTF-GB reactors were conducted to observe the effects of liquid loading on air pressure drop through the media.

Transient loading and profile studies were also conducted during the study. During transient loading, inlet concentrations of C_2H_4 were varied stepwise from 8 to 100 $\mathrm{mg\,m^{-3}}$. The profile study was conducted to measure the C_2H_4 removal according to media bed depths of 5, 25, and 50 cm from the top of the media. Each of transient loading and profile studies lasted only a few hours for reactors BTF-L2, BTF-H2, and BTF-GB2.

Table 2
Operating conditions of bioreactors with normal loading.

Phase	Time (day)	Inlet levels ($\mathrm{mg\,m^{-3}}$)	Liquid recirculation (factor)	Other adjustments
1	0–48			Daily adjusted pH = 7.0
2	48–92		BTF-L and BTF-GB: 1[b] BTF-M: 2[b] BTF-H: 4[b] BF: 2/6[c]	Daily adjusted pH = 7.0 (days ~64) Daily adjusted pH = 7.5 (days 64–78) Daily adjusted pH = 8.0 (days ~76) Backflushing (day 52) New pH buffering (day ~71) Addition of more sodium bicarbonate (days 71 and 77)
3	92–131	Ammonia: 18–29[a] Ethylene: 23–31[a]	BTF-L: 0.5[b] BTF-M: 1[b] BTF-H: 2[b] BF: 2/6[c] BTF-GB: 0.5[b]	Trickle flow rates were reduced in biotrickling filters (BTF-L, BTF-M, BTF-H, and BTF-GB)
4	131–142		BTF-L: 0.5[b] BTF-M: 1[b] BTF-H: 2[b] BTF-H: 4[b] (days 132–141) BF: 1/6 (days 131–132) BF: 2/6[c] BTF-GB: 0.5[b]	
5	142–153	Ammonia: 41–42[a] Ethylene: 31–33[a]	BTF-L: 0.5[b] BTF-M: 1[b] BTF-H: 2[b] BF: 2/6[c] BTF-GB: 0.5[b]	
6	153–162	Ammonia: 15–19[a] Ethylene: 29–32[a]	BTF-L: 0.5[b] BTF-M: 1[b] BTF-H: 2[b] BF: 2/6[c] BTF-GB: 0.5	
7	162–176		BTF-L: 0.5 BTF-M: 1 BTF-H: 2BF: 2/6[c] BTF-GB: 0.5	
8	176–181	Ammonia: Zero Ethylene: 19–25[a]	BTF-X1[d] and BF1: Zero BTF-L2: 0.5 BTF-M2: 1 BTF-H2: 1 BF2: 2/6[c] BTF-GB2: 0.5	Trickle liquid was terminated in BTF-L1, BTF-M1, BTF-H1, BF1, and BTF-GB1

[a] The values are approximated.
[b] Approximate factors were 0.5 for 2.7 $\mathrm{L\,h^{-1}}$, 1 for 5.4 $\mathrm{L\,h^{-1}}$, 2 for 13 $\mathrm{L\,h^{-1}}$, and 4 for 26 $\mathrm{L\,h^{-1}}$.
[c] Factor Y/6 ≈ Factor Y for 10 min intermittently on an hourly basis (with zero liquid flow during the remaining 50 min).
[d] X = L, M, and GB.

2.6. *Statistical analysis*

This study applied the logistic equation [25,26] to describe daily ethylene removal efficiencies. The logistic equation is presented as follows:

$$\frac{1}{Re(t)}\frac{\mathrm{dRe}(t)}{\mathrm{d}t} = F\left(1 - \frac{Re(t)}{Z}\right) \tag{1}$$

The parameters Z and F are the carrying capacity and the rate constant, respectively. There are two equilibria satisfying $\mathrm{d}(\mathrm{Re}(t))/\mathrm{d}t = 0$, at $\mathrm{Re}(t) = 0, Z$. The removal efficiency on day t, $\mathrm{Re}(t)$, should eventually converge to Z as reaction time elapses, and, consequently, the logistic function has an S-shaped curve. The parameter F determines the increasing rate of $\mathrm{Re}(t)$ as it approaches Z.

For reasonable fits of the ethylene removal efficiencies, Eq. (2) requires more terms and is as follows:

$$Re(s,t) = E + \frac{Z(s)\ \exp(F(s)t + T)}{1 + \exp(F(s)t + T)} + \varepsilon \quad \varepsilon \sim i.i.d.N(0, \sigma^2) \tag{2}$$

The parameters $F(s)$ and $Z(s)$ are the characteristic parameters for ethylene removal from a reactor. Index notation s represents an arbitrary reactor (s = BTF-L, BTF-M, . . ., or BTF-GB). Each parameter for a treatment can be compared with that of another. The parameters T and E are the constants, which were specified to be identical for all reactors. The parameter T is a re-parameterization of $Z(s)$ and initial value of Re(s, 0) in Eq. (1), although not characteristic as the $Z(s)$ parameter. The variable t represents a day elapsed with ethylene degradation, and t is equal to zero at day 92. As t increases continuously, ethylene removal Re(s, t) eventually converges to $E + Z(s)$. The parameter $F(s)$ is associated with the rate of increase of Re(s, t). The residual against each predictive value resulting from the equation, ε is assumed to be independent and follow the normal distribution with a mean of zero and a constant variance, σ^2.

There may be potential autocorrelations among the random error terms (ε), but for simplification that was neglected in this model. Ignorance of the autocorrelations may lead to somewhat overestimating of the variance σ^2, which makes the comparisons a little more conservative. Eq. (2) was implemented separately and therefore all of the parameters in Eq. (2) were independently estimated.

This study selected the ethylene removal efficiencies from days 92 to 155 for all of the reactors for the models because the data in the time slots could be characterized as S-shaped. The hypothesis test was to decide the significance of differences in parameter values between two reactors or treatments. The null hypothesis (H_0) was accepted when the result of the pair-wise comparisons showed that the two parameters were not significantly different from each other based on the p-statistic.

Otherwise, the alternative hypothesis (H_1), indicating significant differences, should be accepted while the null hypothesis is rejected. No further test was conducted to decide which parameter was greater. The PROC NLMIXED procedure by SAS® software fitted the nonlinear mixed model [27]. The parameters of $Z(s)$, $F(s)$, E, and T were estimated. The optimal solutions for parameter estimation were obtained using the dual Newton method [28], by which the deviation between experimental and simulated data was minimized. A maximum of 1000 iterations was applied to the program running.

The MODEL statement in SAS® specified the response variables, which for this study were ethylene removal efficiencies. The comparisons were made between pairs of reactors or treatment sets using the estimated parameters.

The significance of difference between parameter values was decided based on the p-statistic of 0.05, but marginal significance was sometimes used with 0.1 of the p-statistic, when no significance was found with 0.05 of the p-statistic for multiple comparisons.

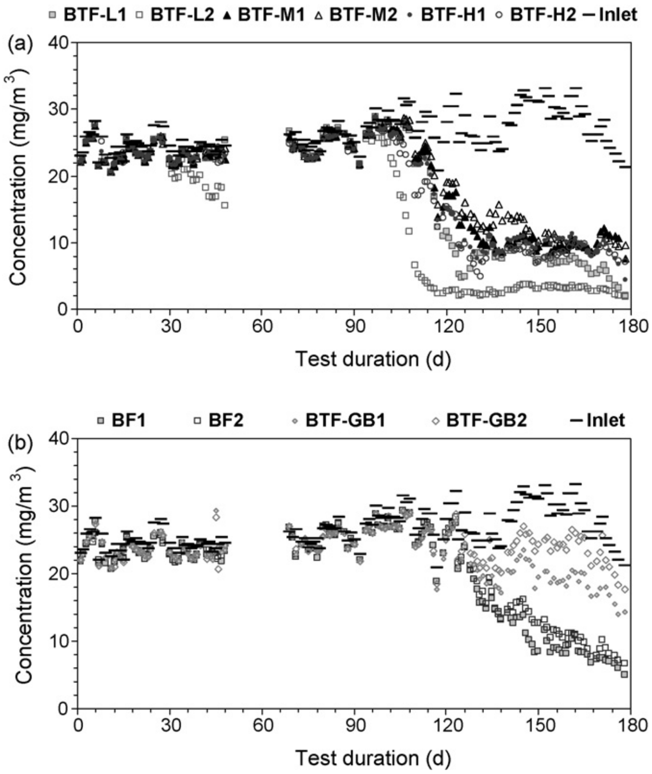

Fig. 3. Daily means of outlet ethylene concentrations for BTF-L, BTF-M, and BTF-H reactors (a), BF and BTF-GB reactors (b). The mean error ranges are 1.25 mg m^{-3} (a) and 1.47 mg m^{-3} (b).

3. Results and discussion

3.1. *C_2H_4 and NH_3 removal under normal loading*

Fig. 3a, b and 4a, b present daily outlet C_2H_4 concentrations and the corresponding removal efficiencies for each reactor. Before day 92, C_2H_4 removal efficiency was close to zero for all of the reactors except BTF-L2. However, removal efficiencies significantly increased after day 92. In particular, the biotrickling filter BTF-L2 achieved markedly high removal efficiencies of approximately 90%. On the other hand, BTF-GB had poor removal efficiencies of less than 50%. The BTF-L1, BTF-M, and BTF-H reactors exhibited relatively similar performances. The C_2H_4 removal of BTF-L1 became superior to that of BTF-H after day 150. The BF reactors did not have a high C_2H_4 removal but continuously increased during the third and the fourth phases. It is noted that biotrickling filters with perlite had greater ethylene removal than BTF-GB and BF. It is probably because the perlite biotrickling filters had a proper nutrition supply through continuous liquid flow, as compared with BF. The higher ethylene removal of perlite biotrickling filters over glass bead biotrickling filters is caused by the high liquid (water and nutrition) and biofilm holding ability of perlite, due to its higher active specific surface compared to glass beads.

Table 3 exhibits the estimated parameters resulting from the data fitting with five treatment sets and Eq. (2). The parameter values range from 0.27 to 0.82 for $Z(s)$ and from 0.10 to 0.27 for $F(s)$. The $Z(s)$ and $F(s)$ reflect how high the ethylene removal efficiency is at the steady-state condition, and how fast the ethylene removal efficiency increases up to $Z(s)$. The symbols of L, M, H, (-), and G rep-

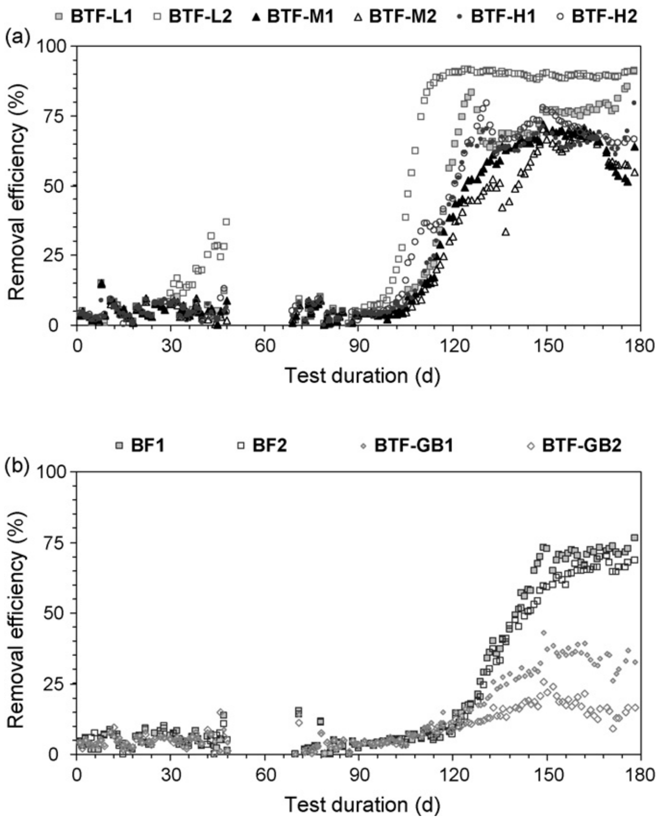

Fig. 4. Daily means of ethylene removal efficiencies for BTF-L, BTF-M, and BTF-H (a), BF and BTF-GB reactors (b). The mean error ranges are 2.75% (a), and 3.42% (b).

resent the respective parameters for BTF-L, BTF-M, BTF-H, BF, and BTF-GB. The symbols SE and DF are defined as the standard deviation and degree of freedom for an estimated value, respectively. The symbols of "Min" and "Max" indicate the minimal and the maximal values of an estimated parameter, which were calculated based on the 95% confidence interval for the standard normal distribution. All parameters seem reasonably estimated. A slightly low t value for the parameter E, which was estimated as a constant for all treatment sets, reflects that initial ethylene removal efficiencies slightly varied among reactors, especially BTF-L.

Table 3
The estimated parameters of $F(s)$ and $Z(s)$, based on the modeling with the five treatment sets.

Parameter	Estimate	SE	Pr > |t|	Min	Max
$F(L)$	0.2665	0.01624	<0.0001	0.2346	0.2984
$F(M)$	0.174	0.01182	<0.0001	0.1508	0.1972
$F(H)$	0.2038	0.01241	<0.0001	0.1794	0.2282
$F(-)$	0.1048	0.01004	<0.0001	0.0851	0.1246
$F(G)$	0.1294	0.01564	<0.0001	0.0987	0.1601
T	−4.6711	0.2912	<0.0001	−5.243	−4.0992
E	0.02975	0.009457	0.0017	0.0112	0.0483
$Z(L)$	0.7736	0.01535	<0.0001	0.7435	0.8038
$Z(M)$	0.5991	0.02079	<0.0001	0.5583	0.64
$Z(H)$	0.671	0.0172	<0.0001	0.6372	0.7048
$Z(-)$	0.8262	0.09284	<0.0001	0.6439	1.0086
$Z(G)$	0.2663	0.03927	<0.0001	0.1891	0.3434
e	0.006754	0.0004	<0.0001	0.006	0.0075

Table 4
The results of multiple comparisons for the parameters $Z(s)$ and $F(s)$ in the model with the five treatment sets.

Label	Estimate	SE	Pr > |t|	Min	Max
$Z(L)–Z(M)$	0.1745	0.01982	<0.0001	0.1356	0.2134
$Z(L)–Z(H)$	0.1026	0.01718	<0.0001	0.06891	0.1364
$Z(L)–Z(-)$	−0.05261	0.08968	0.5577	−0.2288	0.1235
$Z(L)–Z(G)$	0.5074	0.04013	<0.0001	0.4286	0.5862
$Z(M)–Z(H)$	−0.07184	0.021	0.0007	−0.1131	−0.0306
$Z(M)–Z(-)$	−0.2271	0.08917	0.0111	−0.4022	−0.052
$Z(M)–Z(G)$	0.3329	0.04179	<0.0001	0.2508	0.415
$Z(H)–Z(-)$	−0.1553	0.08972	0.0841	−0.3315	0.02096
$Z(H)–Z(G)$	0.4047	0.04074	<0.0001	0.3247	0.4847
$Z(-)–Z(G)$	0.56	0.0964	<0.0001	0.3706	0.7493
$F(L)–F(M)$	0.09249	0.009136	<0.0001	0.07454	0.1104
$F(L)–F(H)$	0.06267	0.008797	<0.0001	0.0454	0.07995
$F(L)–F(-)$	0.1616	0.01033	<0.0001	0.1414	0.1819
$F(L)–F(G)$	0.1371	0.01735	<0.0001	0.103	0.1711
$F(M)–F(H)$	−0.02981	0.007169	<0.0001	−0.0439	−0.0157
$F(M)–F(-)$	0.06916	0.00755	<0.0001	0.05433	0.08399
$F(M)–F(G)$	0.04458	0.01533	0.0038	0.01447	0.07468
$F(H)–F(-)$	0.09897	0.007721	<0.0001	0.08381	0.1141
$F(H)–F(G)$	0.07439	0.01552	<0.0001	0.04391	0.1049
$F(-)–F(G)$	−0.02458	0.01504	0.1026	−0.0541	0.00495

Table 4 shows the results of multiple comparisons for the parameters $F(s)$ and $Z(s)$ between the five treatment sets. The parameters $F(s)$ of BF ($F(-)$) and BTF-GB ($F(G)$) are relatively similar to each other. Those of the parameters $F(s)$ of BTF-L ($F(L)$) and BTF-H ($F(H)$) are higher than those of BF ($F(-)$) and BTF-GB ($F(G)$). On the other hand, the value of the parameter $Z(s)$ of BTF-GB ($Z(G)$) is the lowest among all. The value of the parameter $Z(s)$ of BF ($Z(-)$) is as high as that of BTF-L ($Z(L)$). The parameters $F(s)$ and $Z(s)$ for BTF-L ($F(L1)$, $F(L2)$, $Z(L1)$, and $Z(L2)$) and BTF-H ($F(H1)$, $F(H2)$, $Z(H1)$, and $Z(H2)$) are approximately two times higher than those for BTF-GB, respectively. It is interesting that high ethylene removal efficiencies at the steady-state were predicted for the reactors with the low trickling flow rates (BTF-L and BF), while BF reactors had far lower $F(s)$ which implies slow microbial growth or adaptation.

Fig. 5a–c present the daily means of ammonia inlet concentrations and corresponding removal efficiencies for each reactor. Except for days 0–20 and days 71–80, ammonia removal efficiencies were greater than 90%. The poor performance during those periods was due to low nitrification activity in the microbial adaptation stage for days 0–20 and utilization of sodium bicarbonate to eliminate acidification in the biofilm for days 71–80. The acidification during days 57–70 was due to the increase in microbial activity for ethylene degradation and nitrification.

Ammonia removal efficiencies remained high with inlet ammonia concentrations of greater than 40 $mg\,m^{-3}$ during days 142–153. This was because ammonia, with a higher solubility in water and adsorption capacity to media surface than ethylene, is easily transferred into the liquid phase or media surface on the polar surfaces of perlite and glass beads. Additionally, ammonia can be rapidly degraded in the biofilm phase via nitrification.

A previous study that utilized perlite biofilter medium to eliminate about 15 and 34 $mg\,m^{-3}$ of NH_3 also reported high NH_3 removal efficiencies of greater than 99% by nitrification over 100 days [9]. De heyder et al. [7] reported C_2H_4 gas removal was enhanced with daily dosage of NH_3. Rigler and Zechmeister-Boltenstern [11] observed that the microbial uptake of C_2H_4 and methane was improved by the elevated ammonium concentration in acidic spruce forest soil, but nitrate (NO_3^-), which is the final product of nitrification, inhibited oxidation of C_2H_4 and methane.

The liquid pH was adjusted to 7 or 8 daily, using sodium hydroxide (NaOH) and phosphoric acid (H_3PO_4) to provide an optimal nitrification pH condition of 7.0–8.7. Liquid pH was stably maintained at 6.5 or greater after day 92. Different liquid recirculation rates or the presence of C_2H_4 had no significant effect on NH_3 removal. It is because NH_3 is easy to be degraded and transferred through liquid recirculation flow.

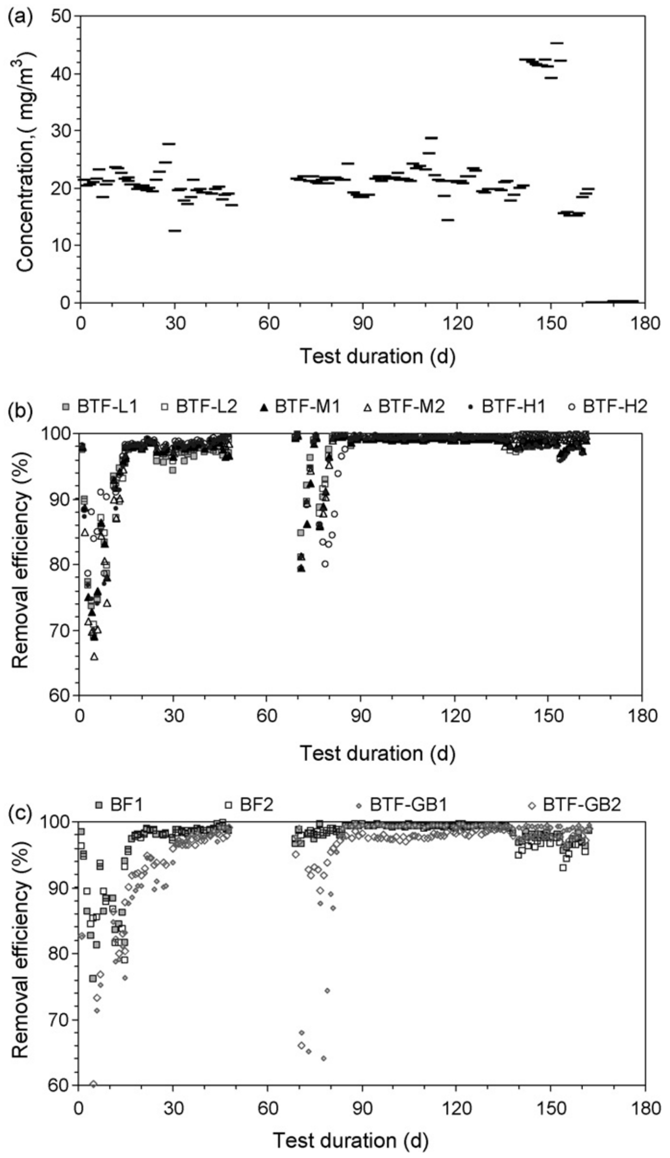

Fig. 5. Daily means of inlet ammonia concentrations (a) and ammonia removal efficiencies for BTF-L, BTF-M, and BTF-H (b), BF and BTF-GB reactors (c). The mean error ranges are 0.37 mg m^{-3} (a), 1.04% (b), and 1.98% (c), respectively.

During days 176–181, liquid recirculation was terminated for reactors BTF-L1, BTF-M1, BTF-H1, BF1, and BTF-GB1 to confirm the effects of the liquid phase on each reactor. The objective of the experimental observation for this short time was to observe the effect of terminating trickle liquid on C_2H_4 removal without any long-term microbial activity factor.

As a result, C_2H_4 removal efficiencies significantly increased for BTF-M1 and BTF-H1 without liquid recirculation as compared with each of their counterpart reactors (Fig. 6). As shown in Table 5, the increase of removal efficiencies was 26% and 17% for BTF-M1 and BTF-H1 between days 176 and 181, respectively. On the other hand, C_2H_4 removal efficiencies in reactor BTF-GB1 decreased from 36.7% to 1% during the same interval. BF1 and BTF-L1 had smaller changes even though liquid was terminated. Other reactors which maintained liquid recirculation during days 176 and 181, i.e. reactors BTF-L2, BTF-M2, BTF-H2, BF2, and BTF-GB2, showed only −5% to 2% change in removal efficiencies between days 176 and 181.

The experimental results show that removal of C_2H_4, which has low solubility in water (131 mg L^{-1} at 20 °C [29]), can be affected by the presence of trickle flow in a reactor. A previous study on ether degradation also reported that removal efficiency of ether, which is also slightly soluble to water, decreased with increasing water content in a biotrickling filter [30]. It was observed that low water content in the media promoted ether diffusion into the biofilm and increases in biofilter performance.

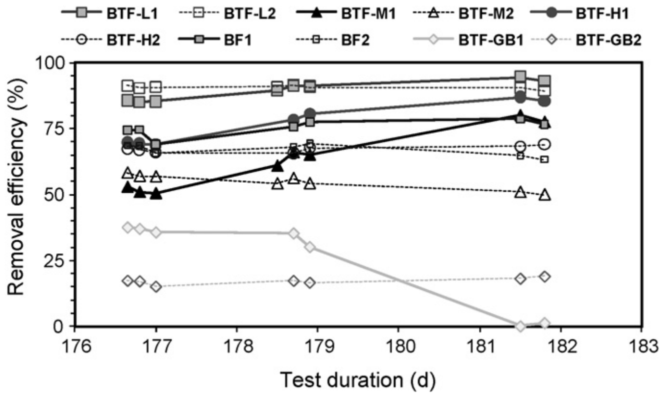

Fig. 6. Ethylene removal efficiencies for each bioreactor during days 176–181. (Liquid recirculation was terminated for BTF-L1, BTF-M1, BTF-H1, BF1, and BTF-GB1.)

Tambwekar et al. [9] also observed increases of C_2H_4 removal efficiency due to mass transfer limitation, as moisture content decreased in the biofilter media. In this study, mass transfer limitation of C_2H_4 or oxygen also existed under the presence of the liquid phase. Due to low liquid recirculation rates, there was only a slight increase of C_2H_4 removal in the BF1 reactor from days 176 to 181. This implies that BF reactors had relatively low mass transfer limitations, and the lower C_2H_4 removal of the reactors was caused by poor distribution of nutrients due to the low trickle liquid amounts inside the bed. The decreasing removal efficiency of C_2H_4 in BTF-GB1 during days 176–181 as plotted in Fig. 6 could be explained by excessive drying of the glass beads due to discontinuance of liquid spray in BTF-GB1, which led to inhibition of microbial activity.

Morales et al. [15] reported that toluene removal efficiencies significantly decreased by drying of the biofilter. In their study, the drying condition was introduced by terminating the inlet relative humidity for several days. The moisture content in the perlite biotrickling filter media in the study described herein included both external water supply and inlet relative humidity of 50–60%, which was sufficient to prevent drying problems in the perlite biotrickling filters. However, the glass bead medium in reactors BTF-GB had low liquid holding capacity due to its nonporous structure, which quickly led to dry media in BTF-GB1 after the discontinuance of the liquid spray.

The differences of C_2H_4 removal efficiencies between the duplicate reactors in each identical set most likely resulted from unequal characteristics of medium pore structure and random behavior of liquid and microbial reactions [31,32].

Table 5
Ethylene removal efficiencies with their corresponding error ranges of each reactor at the end of the biotic experiment (days 176–181). Trickle liquid was terminated for BTF-L1, BTF-M1, BTF-H1, BF1, and BTF-GB1.

	Day 176	Day 178	Day 181	Change (%)
BTF-L1	85.37 (0.34)	90.63 (0.58)	93.81 (0.79)	9.88
BTF-L2	90.82 (0.41)	91.04 (0.38)	89.93 (0.56)	−0.98
BTF-M1	51.53 (1.47)	64.08 (3.08)	78.90 (1.26)	53.12
BTF-M2	57.30 (0.89)	54.80 (0.69)	50.42 (0.47)	−11.99
BTF-H1	69.26 (0.46)	79.42 (1.41)	86.23 (0.75)	24.49
BTF-H2	66.70 (0.73)	66.70 (0.75)	68.63 (0.35)	2.89
BF1	72.75 (1.74)	76.64 (0.78)	77.66 (0.95)	6.75
BF2	67.60 (0.91)	68.69 (0.52)	63.97 (0.84)	−5.38
BTF-GB1	36.77 (0.38)	32.76 (0.45)	0.79 (0.63)	−97.84
BTF-GB2	16.55 (0.84)	16.98 (1.12)	18.59 (0.43)	12.27

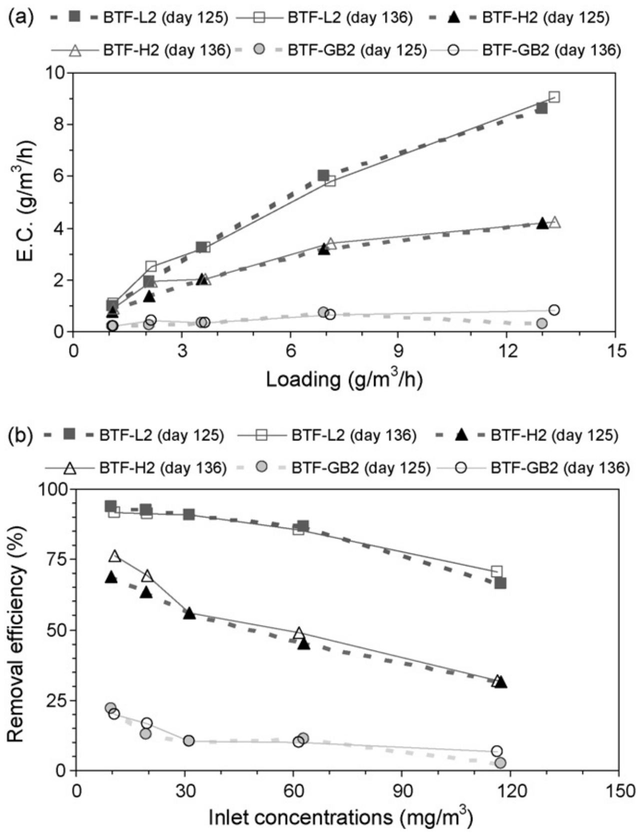

Fig. 7. Elimination capacities of ethylene (a) and removal efficiencies (b) of ethylene at different loading rates on days 125 and 136. The mean error ranges are 0.11 g m^{-3} h^{-1} (a) and 0.89% (b), respectively.

Tambwekar et al. [9] used perlite biofilters to treat 1–14 mg m^{-3} of inlet C_2H_4 with inlet air humidification. Using a short EBRT of 30 s, which was similar to that used in this study, C_2H_4 removal efficiency of 99% was accomplished. Low inlet C_2H_4 levels and good control of moisture content of the medium led to such high performance. They also observed both mass transfer limitation and drying when the media moisture content in media was changed.

Also, biological limitation contributes to the difference among ethylene removal efficiencies due to significant changes in trickle liquid flow rates. Since the liquid recirculation flow was steady and continued over a long-term period, the mass transfer limitation in the long term can affect the growth of ethylene degraders in microbiological biofilms and consequently ethylene removal.

3.2. Transient loading and profile study

The C_2H_4 EC (Elimination Capacity) and RE (removal efficiencies) of BTF-L2, BTF-H2, and BTF-GB2 were plotted against their loading rates in Fig. 7a and b, respectively. The EC and RE of the perlite reactors changed significantly with increasing loading rates, but those of the glass bead reactors changed only slightly. Consequently, BTF-GB2 exhibited very low EC and RE. There was an insignificant difference of C_2H_4 EC or RE between days 125 and 136. Ammonia removal efficiencies of all reactors were greater than 95% on days 125 and 136.

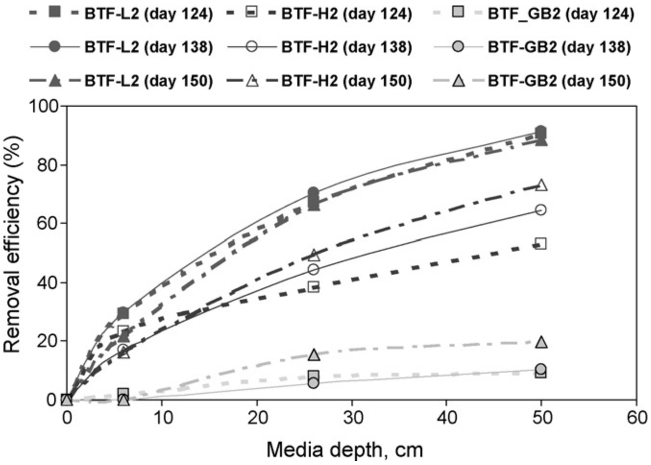

Fig. 8. Transformed data on ethylene removal efficiencies as a function of media depth (a) day 124, (b) day 138, and (c) day 150. The mean error range is 1.35%.

Fig. 8 shows the ethylene removal efficiencies resulting from the profile study in BTF-L2, BTF-H2, and BTF-GB2 reactors on days 124, 138, and 150, respectively. The bed depths for the gas sampling were 5, 25 and 50 cm from the top of each reactor. Reactors BTF-L2 and BTF-GB2 had the highest and the lowest removal efficiencies along the entire profile depth, respectively. At a greater media depth, there was only a slight difference in removal efficiencies between BTF-L2 and BTF-H2, and the difference increased as the media depth increased. BTF-GB2 performed poorly in the upper part of the media (i.e. at lower media depth). Unlike C_2H_4 degradation, about 90% of the inlet NH_3 in BTF-L2 and BTF-H2 was removed within 0–5 cm of media depth. This indicated that most of the NH_3 entering each perlite media reactor was easily removed. Consequently, its degradation occurred along the entire depth of the media.

3.3. Outlet carbon dioxide (CO_2) and air pressure drop

Fig. 9 shows the measured outlet or inlet CO_2 concentrations averaged over 5–8 days. The resultant CO_2 levels were roughly

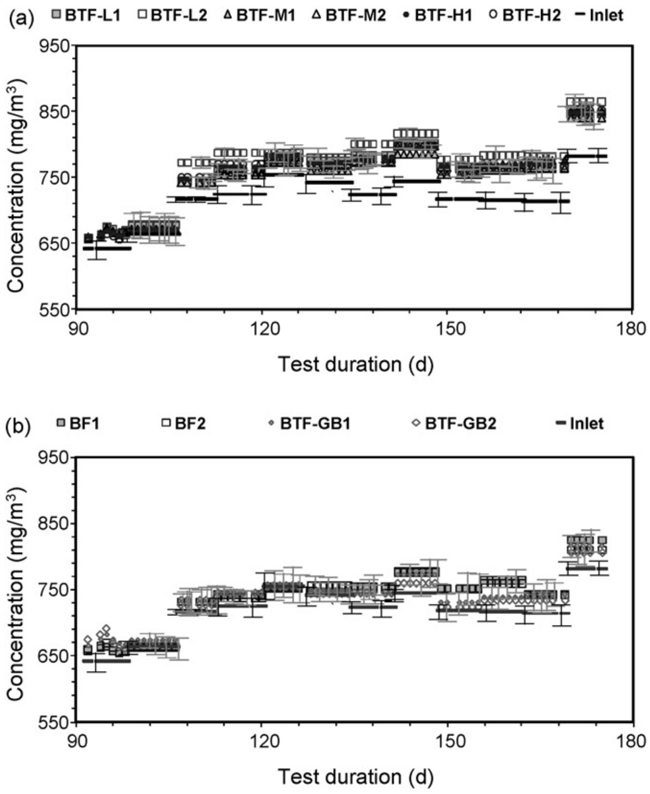

Fig. 9. Outlet concentrations of carbon dioxide averaged over 5–7 days for the reactors of BTF-L, BTF-M, and BTF-H (a), and BF and BTF-GB (b). The error bars are presented in the averaged data.

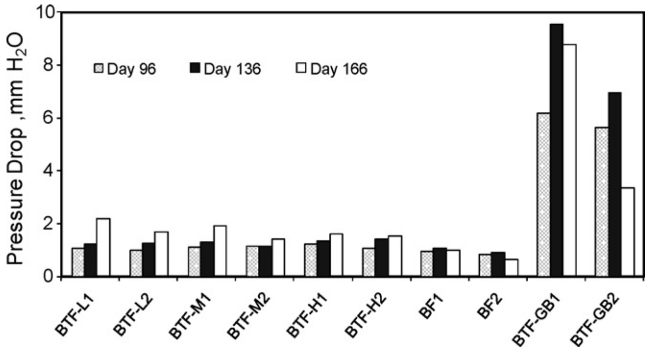

Fig. 10. Pressure drops according to days elapsed for each reactor.

correlated with C_2H_4 removal. For example, reactor BTF-L2, which exhibited the highest C_2H_4 removal efficiencies, produced the highest quantities of CO_2. On the contrary, reactors BTF-GB with the lowest C_2H_4 removal efficiencies generated the lowest levels of CO_2. C_2H_4 may be converted into CO_2 as an end product of microbial oxidization under aerobic conditions [9], which is consistent with the findings in this study. Generally, some carbon molecules in the contaminants may be utilized for microbial biofilm construction for microbial growth and others may be converted into CO_2 production [33].

Although the nitrifiers in each reactor could utilize CO_2 as a carbon source, the outlet concentrations of CO_2 from each reactor were not highly affected by termination of the ammonia supply and rather increased due to increased C_2H_4 removal. Actually, as shown in a previous section (Section 2.3), fresh liquid contains $1\,g\,L^{-1}$ of bicarbonate, enough to be used as carbon source in ammonia nitrification for 7 days; the ammonia loading rates were approximately 2–4 g for 7 days ($20–40\,mg\,m^{-3} \times 7\,L\,min^{-1} \times 1440\,day\,min^{-1} \times 7$ days).

Fig. 10 exhibits the pressure head loss along the entire media depth for each reactor, measured on days 96, 136, and 166. Air pressure drop along a filter media depends on the characteristics of the medium such as packing depth, porosity and pore size as well as biofilm mass [34].

The glass beads, which were used in BTF-GB, were tightly packed, and therefore the pressure drop of glass beads was higher than that of perlite. Furthermore, the pressure drop most likely increased in BTF-GB at the end of the experiment, probably due to the clogging caused by biofilm growth in the interstitial volumes inside the media [35]. A short-term variation of the liquid recirculation produced no effect on pressure drop. On the other hand, only a slight increase of pressure drop, due to biofilm growth, for each perlite-based filter was observed, as shown in Fig. 10.

4. Conclusions

Removal efficiencies of C_2H_4 increased for each reactor under stable pH values of 6.5–8.5. However, as the time elapsed, C_2H_4 removal varied widely according to liquid recirculation rates, media type, inlet C_2H_4 level, and media depth. One of the perlite-based biotrickling filters (BTF-L2) accomplished approximately 90% of C_2H_4 removal efficiency with $2.7\,L\,h^{-1}$ (velocity of $0.4\,m\,h^{-1}$) of liquid recirculation. On the other hand, other biotrickling filters had relatively low C_2H_4 removal, probably due to high mass transfer limitation due to a trickle liquid flow higher than $5.4\,L\,h^{-1}$ (velocity of $0.8\,m\,h^{-1}$) or a low media surface area available for microbial biofilm formation. In spite of the lowest liquid recirculation flow rate, BF reactors had lower C_2H_4 removal efficiencies than perlite biotrickling filters, probably because of poor microbial growth or adaptation due to insufficient nutrient supply. In conclusion, perlite biotrickling filtration with continuous but low trickling flow rates that is less than $5.4\,L\,h^{-1}$ (velocity of $0.4\,m\,h^{-1}$) is thought to be the most desirable reactor type for ethylene biofiltration.

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