Journal of Hazardous Materials 250–251 (2013) 190–197

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

A comparative study of fungal and bacterial biofiltration treating a VOC mixture

José M. Estrada[a,b,1], Sergio Hernández[c], Raúl Muñoz[b,1], Sergio Revah[a,*]

[a] Departamento de Procesos y Tecnología, Universidad Autónoma Metropolitana-Cuajimalpa, Artificios 40, Col. Miguel Hidalgo, Delegación Álvaro Obregón, Mexico
[b] Departamento de Ingeniería Química y Tecnología del Medio Ambiente – Universidad de Valladolid, Valladolid, Spain
[c] Departmento de Procesos e Hidráulica – Universidad Autónoma Metropolitana – Iztapalapa Mexico D.F. Mexico

HIGHLIGHTS

- Bacterial biofilter showed better EC and ΔP than fungal biofilter.
- The preferential biodegradation order was: propanal > hexanol > MIBK > toluene.
- Propanal partially inhibited the biodegradation of the rest of VOCs.
- The two-stage biofilter showed a higher stability than the individual units.

ARTICLE INFO

Article history:
Received 14 December 2012
Received in revised form 24 January 2013
Accepted 28 January 2013
Available online xxx

Keywords:
Biofiltration
Fungal biofilter
Gas treatment
Propanal
MIBK
Hexanol
Toluene
Volatile organic compounds

ABSTRACT

Bacterial biofilters usually exhibit a high microbial diversity and robustness, while fungal biofilters have been claimed to better withstand low moisture contents and pH values, and to be more efficient coping with hydrophobic volatile organic compounds (VOCs). However, there are only few systematic evaluations of both biofiltration technologies. The present study compared fungal and bacterial biofiltration for the treatment of a VOC mixture (propanal, methyl isobutyl ketone-MIBK, toluene and hexanol) under the same operating conditions. Overall, fungal biofiltration supported lower elimination capacities than its bacterial counterpart (27.7 ± 8.9 vs 40.2 ± 5.4 g C m^{-3} reactor h^{-1}), which exhibited a final pressure drop 60% higher than that of the bacterial biofilter due to mycelial growth. The VOC mineralization ratio was also higher in the bacterial bed (≈63% vs ≈43%). However, the substrate biodegradation preference order was similar for both biofilters (propanal > hexanol > MIBK > toluene) with propanal partially inhibiting the consumption of the rest of the VOCs. Both systems supported an excellent robustness versus 24 h VOC starvation episodes. The implementation of a fungal/bacterial coupled system did not significantly improve the VOC removal performance compared to the individual biofilter performances.

1. Introduction

The increasing need for economic and sustainable technologies to abate odors and industrial gaseous pollutants has gradually shifted the attention to biological waste gas treatment technologies [1,2]. Despite the wide range of bioreactor configurations, (e.g. biofilter, biotrickling filters, bioscrubbers, activated sludge diffusion, two-phase partitioning systems, etc.), conventional biofilters still constitute the most commonly implemented technology at full scale due to their relative simplicity, lower investment costs and the extensive experience gained in their design and operation over the last 20 years [3].

In general, biofiltration activity is mainly due to bacteria which exhibit a high diversity and versatility when treating VOC mixtures [4–6]. However, despite that bacterial biofilters have been reported as a robust technology for off-gas treatment, their performance rapidly deteriorates at low moisture contents, low pH values and nutrients limiting scenarios [7]. On the other hand, fungal biofiltration has been claimed to better withstand these harsh environmental conditions [8,9]. In addition, the fungal composition and its mycelial aerial growth can significantly increase the mass transfer of hydrophobic VOCs from the gas phase to the biomass [10]. Hence, VOCs such as toluene, styrene, α-pinene or hexane have been successfully treated in fungal biofilters at unprecedentedly high elimination capacities [11–14] despite the fact that fungi have lower specific degradation rates [15]. However, extensive fungal biomass growth, may lead to packing media clogging which has been reported to be the most important drawback in fungal biofiltration, particularly at high VOC concentrations [11,16]. Despite the recent advances on the understanding of both fungal and bacterial biofiltration, there is a lack of systematic comparative studies assessing their performance under identical operational conditions, especially when a mixture of pollutants is studied.

* Corresponding author. Tel.: +52 55 2636 3801x3832; fax: +52 55 2636 3800.
E-mail address: srevah@xanum.uam.mx (S. Revah).
[1] Tel.: +34 983186424; fax: +34 983423013.

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.01.064

The present work compared the performance of a fungal and a bacterial biofilter for the treatment of a complex VOC mixture. Their response was compared to that of a hybrid system, consisting of a bacterial biofilter in series with a fungal biofilter.

2. Materials and methods

2.1. Microorganisms

The fungal biofilter was inoculated with fungal biomass from a seed biofilter inoculated with *Paecilomyces variotii* and treating the same VOC mixture used in this study. Inoculation was conducted by mixing 50% of the packing material from the seed biofilter with 50% of sterilized perlite in a sterile chamber. The initial fungal biomass concentration in the biofilter was 4.1 g VSS L^{-1} bed. The bacterial biofilter was inoculated with aerobic activated sludge from the wastewater treatment plant attain a final concentration of 0.7 g VSS L^{-1} bed.

2.2. Chemicals and mineral salt medium

Propanal and hexanol with purity higher than 97% (reagent grade) were purchased from Sigma–Aldrich (Germany). Methyl Isobutyl Ketone (MIBK) and toluene were purchased from Reasol (México) with a 99.5% purity. The mineral salt medium (MSM) used for irrigation in both biofilters was described by Vergara-Fernández et al., 2012 with the only modification of 6 instead of 18 g l^{-1} $NaNO_3$ [17]. The pH was adjusted to 4.0 with HNO_3 for the irrigation of the fungal biofilter and to 7.0 with NaOH for the bacterial biofilter. The antibacterial agent Chloramphenicol (0.5 g L^{-1}) (Sigma–Aldrich, USA) was added to the MSM used for the irrigation of the fungal biofilter.

2.3. Experimental setup

Two glass columns of internal diameters 7.8 and 7.2 cm were used as fungal and bacterial biofilters, respectively (See supporting material Figure S1). Both columns were filled with sterile vermiculite (particle size 2.4–5.0 mm) to a final working volume of 2 L. Both packing media were then soaked with their corresponding MSM to obtain a 60% moisture and a wet packing density of 400 g L^{-1}.

The gaseous VOC mixture was obtained by addition of liquid propanal, MIBK and toluene using a syringe pump into a mixing chamber where the VOCs evaporated in a continuous air flow of 320 mL min^{-1}. An air stream, (0.290 L min^{-1}), saturated with hexanol vapor was combined with the main VOC-laden stream and the mixture further diluted with 3.4 L min^{-1} of water-saturated air to attain the target VOC concentrations (Propanal = 0.65 ± 0.16 g m^{-3}, MIBK = 0.96 ± 0.25 g m^{-3}, toluene = 0.99 ± 0.27 g m^{-3} and hexanol = 0.17 ± 0.04 g m^{-3}). Total organic C loading rate applied was 105.4 ± 23.8 g C m^{-3} reactor h^{-1} and 104.8 ± 20.5 for the fungal and bacterial biofilters, respectively. Finally, the water-saturated VOC stream was equally split and fed in parallel to the fungal and bacterial biofilters for 60 days. The operational strategy was the same for both biofilters: a startup period of 11 days with an empty bed residence time (EBRT) of 90 s to allow for microbial acclimation. The EBRT was then reduced to 60 s and maintained thereafter. On day 19, the air flow was reversed in both biofilters from a downwards to an upwards configuration to promote better biomass distribution. On day 48, propanal was removed from the VOC mixture to assess its influence on the biodegradation of the other VOCs. Biofilter irrigation (150 mL of pH adjusted MSM) was performed intermittently until day 32 and afterwards every five days. The pH of the leachate was measured and re-adjusted before recycling it when pH values fell below 5 in the bacterial biofilter leachate in order to avoid a pH-mediated inhibition and the proliferation of fungal communities. The pressure drop was weekly measured in both biofilters with a manual differential pressure meter.

At day 60, a series configuration was set by connecting the inlet of the fungal biofilter to the outlet of the bacterial biofilter. The entire water-saturated VOC stream (4.0 L min^{-1}) was fed to this combined system, which resulted in an overall EBRT of 1 min (30 s in each reactor). The VOC concentrations were adjusted to maintain a total carbon loading rate of 96.3 ± 4.9 g C m^{-3} reactor h^{-1} (Propanal = 0.47 ± 0.07 g m^{-3}, MIBK = 0.74 ± 0.07 g m^{-3}, toluene = 0.75 ± 0.07 g m^{-3}, hexanol = 0.13 ± 0.03 g m^{-3}). Results from the biofiltration experiments are expressed in terms of inlet loading rate, biofilter elimination capacity (EC) and percent removal efficiency (RE) as previously described [12].

2.4. VOC starvation experiment

An interruption of the VOC supply (while maintaining the air flow) to both biofilters was carried out on day 41 for 24 h to characterize the VOC desorption/adsorption dynamics and the recovery of the biodegradation performance following VOC supply. Both the total organic carbon and CO_2 concentrations were continuously monitored at the gas outlet of both systems during the experiment.

2.5. Analytical procedures

The VOC concentration was analyzed by GC-FID as described by García-Peña et al., 2008 [18] The total organic carbon concentration in the biofilter outlet during the VOC starvation experiment was measured with a PID Continuous Gas Monitor PI 201, HNU Systems Inc., previously calibrated with the VOCs mixture. CO_2 concentration was measured in an infra-red ZRH Fuji Electric analyzer (California Analytical Instruments) calibrated from 0 to 2000 ppm with N_2. When CO_2 concentrations exceeded that range an infra-red ZFP-9 analyzer (California Analytical Instrument) was employed.

The identification of the bio-degradation intermediates was carried out by solid phase micro extraction (SPME). A carboxen/polydimethylsiloxane (PDMS) fiber (Supelco, USA) was exposed for 3 min to the headspace of a 1.5 mL gas-tight vial containing 0.5 mL of the liquid sample. The liquid samples analyzed included the irrigation leachates and the outlet gas condensates (obtained by cooling the outlet stream to 4 °C) of both biofilters on days 47 and 67 (day 6 of in-series operation). The SPME fiber was then desorbed in a 6890 GC (Agilent Technologies) equipped with an Agilent 19091S-433 capillary column and a mass spectrometry detector MS 5975B VL MSD (Agilent Technologies). The injector temperature was maintained at 300 °C while the initial oven temperature steadily increased at 10 °C min^{-1} from 60 °C up to 140 °C. The total column flow was 23.1 mL min^{-1}, MS source temperature 230 °C and the quadrupole temperature 150 °C.

3. Results and discussion

3.1. Fungal biofilter

An intensive growth of the fungal biomass was observed from day 0 to day 11 concomitant with an increase in the total EC, which reached a maximum of 52 g C m_{bed}^{-3} h^{-1} on day 6. Complete biodegradation of propanal was observed from day 1 (Fig. 1 A), which can be attributed to the fact that the fungal inoculum was obtained from a biofilter treating the same VOC mixture and preferentially degrading propanal. The REs for MIBK increased during the first three days of operation up to a maximum of 73%, but

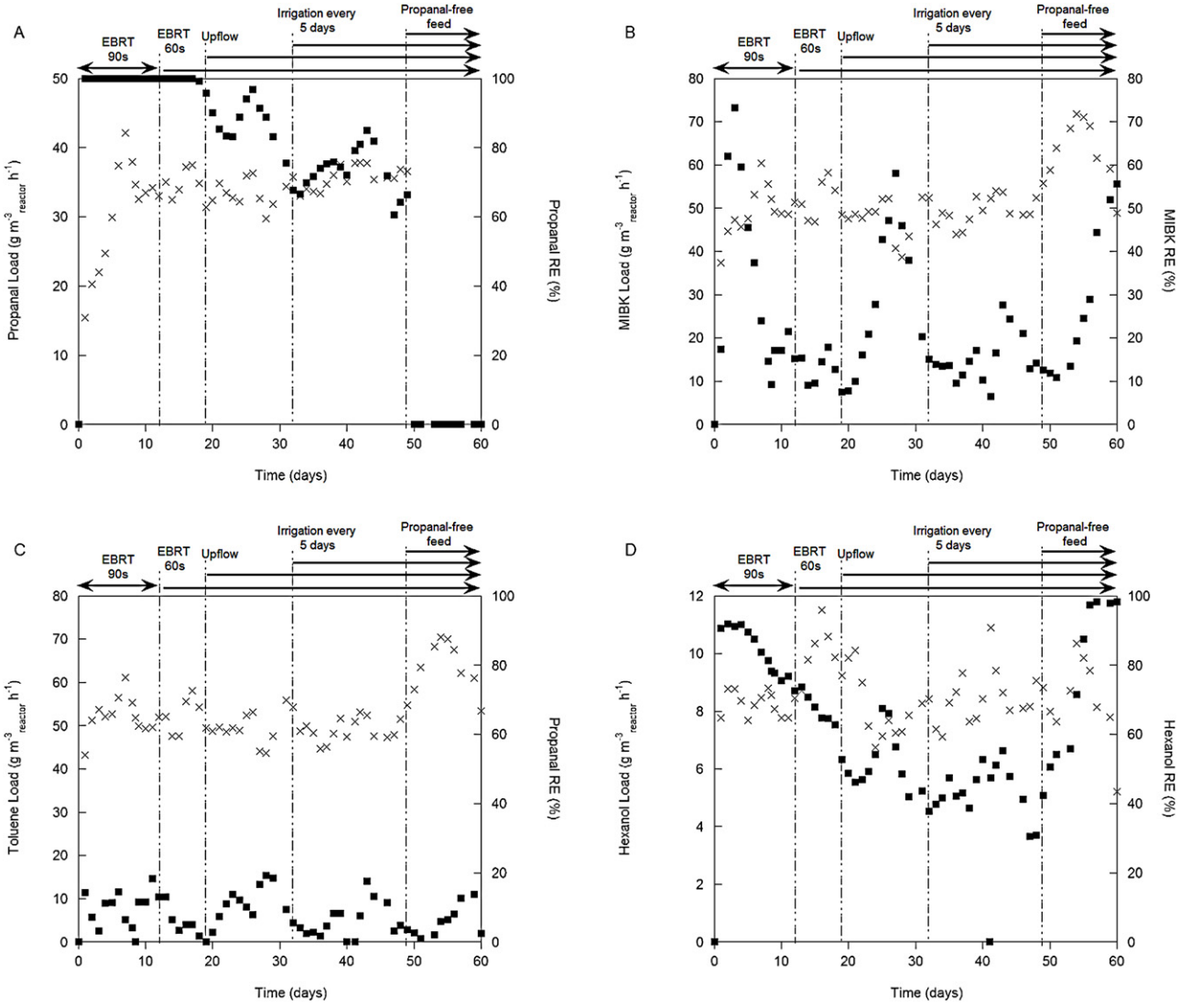

Fig. 1. Time course of the loading rate (×) and RE (■) of propanal (A), MIBK (B), toluene (C) and hexanol (D) in the fungal biofilter. Vertical dash-dotted lines indicate the changes in the operating conditions.

decreased afterwards to remain stable at 15.0 ± 5.3% (Fig. 1 B). Toluene biodegradation during the start-up period, as well as during the entire experiment, was poor and remained always below 20% (Fig. 1C). Hexanol was also efficiently degraded during the first 5 days of operation (RE of 91.0 ± 1.0%) but its removal started to decrease linearly from day 5 (Fig. 1D). The reduction of the EBRT from 90 to 60 s did not have a significant impact on the degradation of any of the target VOCs: propanal was fully depleted, MIBK degraded at ≈15%, toluene removal remained lower than 20% and the deterioration in hexanol biodegradation continued at similar rates.

The inversion of the gas flow direction on day 19 mediated an initial decrease in the RE of all treated VOCs, followed by a rapid recovery in the elimination of propanal, MIBK, toluene and hexanol. This change in the operational configuration of the biofilter promoted a more regular biomass distribution (by visual observation), with the subsequent increase in the total EC. Toluene EC also increased during this biomass growth period but remained below 20% (Fig. 1C), which confirmed the previously reported biodegradation preference pattern: oxygenated compounds > aromatic compounds [19]. VOC hydrophobicity might play an important role in the observed elimination pattern, since the preferred compounds, propanal and hexanol, also presented the lowest dimensionless Henry's Law constants (7.7×10^{-4} and 3.2×10^{-3} C_g/C_l, respectively), which might have resulted in higher mass transfer rates than those for MIBK and toluene ($H = 0.014$ and 0.27, respectively) [20]. However, the fluctuating elimination capacities of MIBK and hexanol recorded at constant VOC loading rate, suggest that microbial activity rather than mass transfer governed the biodegradation process in the fungal biofilter.

The periodical irrigation of the fungal biofilter every 5 days allowed for process stabilization, likely due to supplement of water and nutrients, and an enhanced washout of the accumulated metabolites. Under these operational conditions, the removal efficiencies achieved for propanal, MIBK, toluene and hexanol were 72.8 ± 6.6%, 15.0 ± 5.3%, 5.8 ± 4.7%, 43.4 ± 6.7%, respectively. On day 49, the polluted gas stream was deprived from propanal to assess the performance of the microbial community in the absence of the preferentially biodegraded VOC. Under this new operational scenario, hexanol RE rapidly increased up to an average of 96.0 ± 4.5% from day 56 (Fig. 1D), while MIBK biodegradation gradually improved from day 54 (five days after propanal supply was stopped) to finally achieve a RE of 56% on day 60. Despite that an increase in the toluene RE was also observed, the maximum RE achieved remained within the fluctuation range

Table 1
Average performance of the fungal, bacterial and two-stage biofilters during steady state periods (days 31–49 for fungal and bacterial biofilters and days 6–20 in two-stage biofilter).

Parameter	Fungal	Bacterial	Two stages
Loading rate ($g\,C\,m^{-3}$ reactor h^{-1})	110.2 ± 12.0	108.2 ± 8.1	98.0 ± 9.2
Average EC ($g\,C\,m^{-3}$ reactor h^{-1})	27.7 ± 8.9	40.2 ± 5.4	38.4 ± 8.0
C eliminated (%)	25.1 ± 10.2	37.1 ± 13.1	39.2 ± 8.9
C to CO_2 conversion (%)	45.9 ± 15.8	63.1 ± 11.5	86.9 ± 12.4
Pressure drop increase[a] ($Pa\,m^{-1}$ bed)	91–912	91–372	1398–2003

[a] Pressure drop values account for the complete experimental period.

observed along the entire biofilter operation (Fig. 1D). Based on the results, a particular VOC biodegradation preference order can be established as follows: propanal > hexanol > MIBK > toluene. In this context, the occurrence of competitive inhibition among VOCs has been already described for fungi treating BTEX mixtures. For instance, García-Peña et al. (2008) described the preferential removal of toluene by *P. variotii* in the presence of benzene, ethyl-benzene and xylenes, which confirms that substrate competition is clearly VOC-specific [18]. On the other hand, the total C elimination capacities when propanal was removed remained similar to the previous steady state in the presence of the 4 VOCs ($23.8 \pm 12.2\,g\,C\,m^{-3}$ reactor h^{-1} *vs* $27.7 \pm 8.9\,g\,C\,m^{-3}$ reactor h^{-1}, respectively). The average carbon EC in the fungal biofilter ($27.7 \pm 8.9\,g\,C\,m^{-3}$ reactor h^{-1}) (Table 1) was in the range reported by García-Peña et al., 2008 (10–60 $g\,C\,m^{-3}$ reactor h^{-1}) at a loading rate of $250\,g\,C\,m^{-3}$ reactor h^{-1} (2.5 times higher than in the present study) in a *P. variotii* biofilter treating toluene or benzene.

Despite that high pressure drop, caused by the occupation of the free space by the mycelia, has been commonly pointed out as one of the main drawbacks of fungal biofiltration [16], the maximum pressure drop reached in the fungal biofilter after 60 days of operation was 912 $Pa\,m^{-1}$ bed, which is an acceptable value for industrial biofiltration. Nevertheless, the final pressure drop in the fungal biofilter was approx. three times higher than the one recorded in the bacterial biofilter (Table 1).

3.2. Bacterial biofilter

Complete biodegradation of propanal was observed on day 11 in the bacterial biofilter for a 90 s EBRT after an initial period of rapid biodegradation followed by deterioration at day 5 and a final recovery of the biodegradation performance, which can be attributed to the acclimation of the inoculum to the pollutant mixture (Fig. 2A). The RE of MIBK and toluene remained low during this acclimation period and started to increase after the first week of operation (Fig. 2B, C). Finally, hexanol removal followed a similar trend to that of propanal during the acclimation period, to eventually become stable at RE ≈90% from day 11 (Fig. 2D). The decrease in the EBRT from 90 to 60 s did not have a significant impact on the elimination of propanal and hexanol, however MIBK and toluene achieved maximum removal efficiencies shortly after the EBRT was reduced (63.7% day 14, 100% day 13, respectively) followed by a sharp decrease in their abatement. This increase in MIBK and toluene at this reduced EBRT suggest that the bacterial biofilter was likely limited by microbial activity and the bacterial population totally acclimated, from the initial inoculation with activated sludge, during process operation at 60 s of EBRT. The decrease observed in MIBK and toluene RE from day 17 could not be attributed to nutrients or water content limitations since the irrigation with MSM performed on day 17 did not alleviate this deterioration.

Once the direction of the flow was inverted on day 19, an intensive biofilm growth was also observed all along the bed height in previously non-colonized zones, concomitant with an increase in the RE of MIBK, toluene and hexanol. This enhancement in the biodegradation performance was most significant in the case of MIBK, where REs increased from 10% to 70% by days 26 and 27. However, similarly to the fungal biofilter this temporary enhancement in the abatement performance was followed by decay in the degradation of MIBK, toluene and hexanol, which might be related to the accumulation of metabolites (Fig. 2). In this context, the characterization of the metabolites revealed the presence of 1-propanol and hexanal in both biofilters (see the Metabolites Identification section). In this context a cross inhibition effect might be hypothesized in the bacterial biofilter, where the average EC recorded during this stable period ($40.2 \pm 5.4\,g\,C\,m^{-3}$ reactor h^{-1}) was lower than the ECs commonly reported for conventional biofilters. This effect was more remarkable for toluene, where ECs higher than $100\,g\,m^{-3}$ reactor h^{-1} are commonly reported [21,22], while in this study the toluene EC never exceeded $48\,g\,m^{-3}$ reactor h^{-1}. When the feed stream was deprived from propanal (day 49), a fast increase in the RE of the remaining VOCs was observed, confirming the ability of the community to degrade them. A partial catabolic repression might be involved in the observed reduction in activity since the generalist microbial communities found in biofilters are often able to shift their metabolism in order to degrade all available pollutants under substrate-limited scenarios, while preferentially degrading some specific VOCs under non-limiting substrate conditions [23,24]. In our particular experiment, biofilter feeding with the four VOCs likely resulted in a non-limiting substrate scenario. However, when the system was deprived from propanal (the most easily transferable VOC based on its hydrophilic nature), the substrate availability in the biofilm was likely reduced despite the increase in the loading rate to restore similar carbon loadings, promoting the catabolism of the remaining VOCs. In addition, the fact that the total carbon EC remained similar in the presence and absence of propanal supports the hypothesis of a gradual shift in the metabolism to cover the bacterial carbon and energy needs.

Overall, the bacterial biofilter performed better than the fungal biofilter under stable operating conditions for all tested VOCs (Table 2). These findings can be attributed to the higher microbial diversity presumably established on bacterial biofilters inoculated with activated sludge despite the fact that they have been reported to show reduced mass transfer conditions when compared to fungal biofilters [9]. Recent studies have reported a high microbial diversity in biofilters treating gaseous VOCs mixtures [4,5], and the key role of biodiversity on the robustness and performance of biofiltration processes [25]. The VOC mineralization ratio also constitutes a relevant parameter for the comparison of both biofiltration systems. Thus, while the fungal biofilter converted only a $45.9 \pm 15.8\%$ of the C eliminated to CO_2, this ratio increased up to

Table 2
Average VOC-removal efficiency in the fungal, bacterial and two-stage biofilter during steady state periods (days 31–49 for fungal and bacterial biofilters and days 6–20 in two-stage biofilter).

Pollutant	Fungal	Bacterial	Two stages
Propanal	72.8 ± 6.6%	100.0 ± 0.0%	100.0 ± 0.0%
MIBK	15.0 ± 5.3%	25.4 ± 4.8%	30.0 ± 8.5%
Toluene	5.8 ± 4.7%	9.4 ± 4.1%	13.1 ± 6.4%
Hexanol	43.4 ± 6.7%	90.6 ± 4.1%	90.2 ± 3.1%

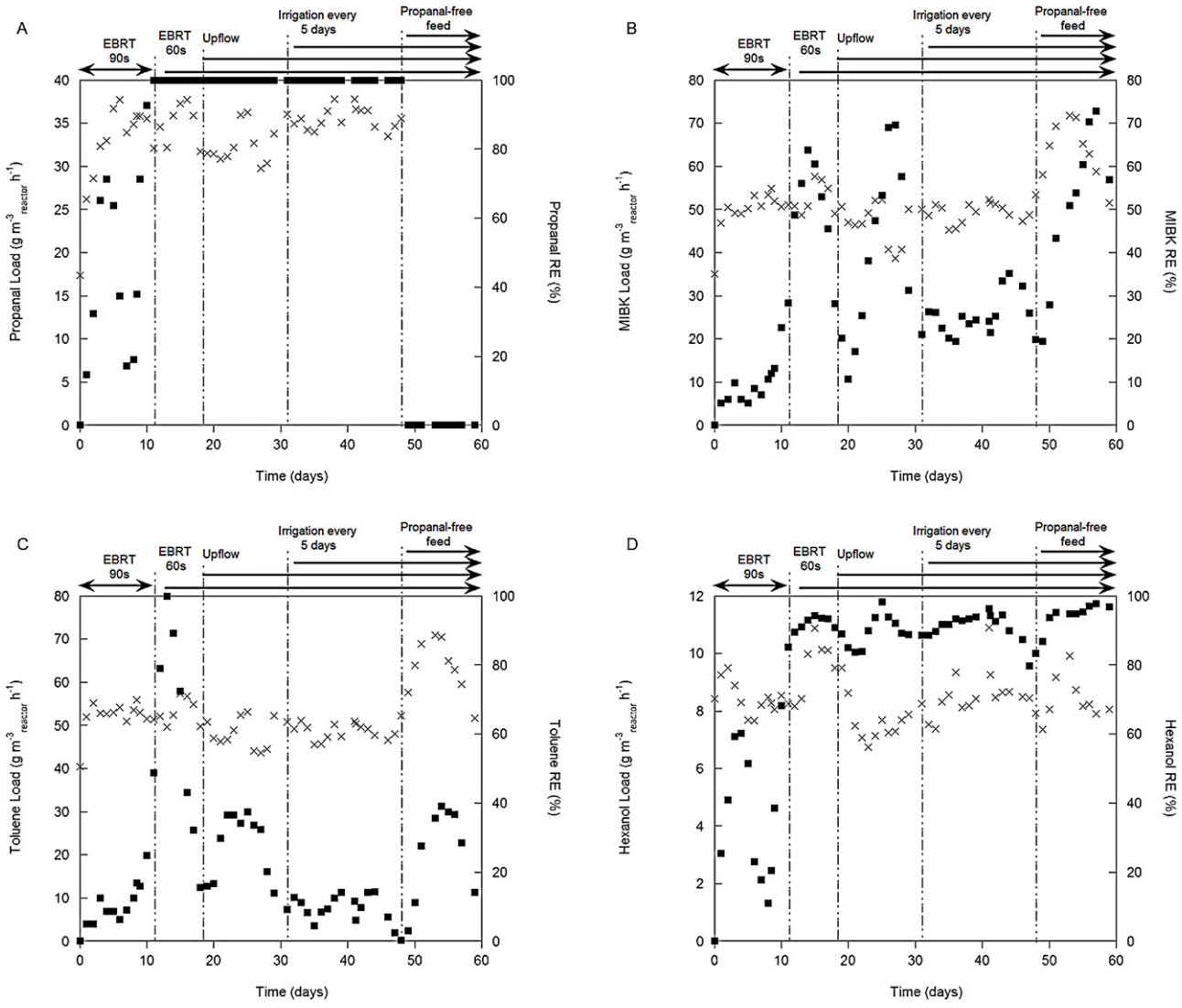

Fig. 2. Time course of the loading rate (×) and RE (■) of propanal (A), MIBK (B), toluene (C) and hexanol (D) in the bacterial biofilter. Vertical dash-dotted lines indicate the changes in the operating conditions.

63.1 ± 11.5% in the bacterial biofilter (Table 1). This suggests that the bacterial community was more efficient oxidizing carbon than the fungal community which showed higher biomass production. Moreover, the presence of mites in the bacterial biofilter but not in the fungal biofilter, which was confirmed by microscope observation of biofilm samples (See supporting material Figure S2), may have also contributed to the higher mineralization rates recorded in the bacterial biofilter and a lower increase in the pressure drop [26]. In terms of pressure drop, bacterial biofiltration exhibited final values 60% lower than those of fungal biofiltration, which is a significant figure from an economic viewpoint. In our particular case, the savings derived from the installation of a bacterial rather than a fungal biofilter after 20 years of operation would account for approx. 0.24 million€ (12,000 € $year^{-1}$).

3.3. Process response to VOC starvation

The concentration of organic C detected at the outlet of both biofilters did not decrease to zero immediately after the interruption of the VOC supply and gradually declined likely due to the desorption of the VOCs or bioreactor intermediates accumulated in the biofilter packing bed. Thus, the full desorption of the volatile organic C present in the fungal biofilter occurred in about 1.5 h (Fig. 3 A), while only 1 h was necessary in the bacterial biofilter to fully desorb all volatile organic carbon (Fig. 3 B). These findings confirmed the fact that more organic C was indeed retained in the fungal biofilter, which can be explained by the high affinity of fungi for hydrophobic VOCs and the aerial mycelia promoting the sorption of organics in the fungal biomass [10]. Surprisingly, the interruption in the VOC supply did not have a major impact in the CO_2 outlet concentrations for the 24 h in the absence of VOCs, which decreased from 853 to 606 ppm (compared to 447.2 ± 48.9 ppmv recorded in air) in the fungal biofilter (≈38%) (Fig. 4 A) and from 1506 to 994 ppm in the bacterial biofilter (≈52%) (Fig. 4 B). This sustained high CO_2 production in both biofilters in the absence of external C supply (based on the inert nature of the support) can be attributed to the metabolism of accumulated reserves and non-volatile metabolites. The presence of mites in the bacterial biofilter may have contributed to the sustained CO_2 production by promoting the bacterial biomass turnover.

When VOC supply was restored, the outlet concentration of organic C increased sharply up to a maximum of 1.45 g m^{-3} in both biofilters 9 min after feed resumption. Then, this concentration rapidly decreased in both biofilters probably due either to the fast kinetics of VOC adsorption in the packing material (commonly observed during process start-up in biofilters) or to an increased

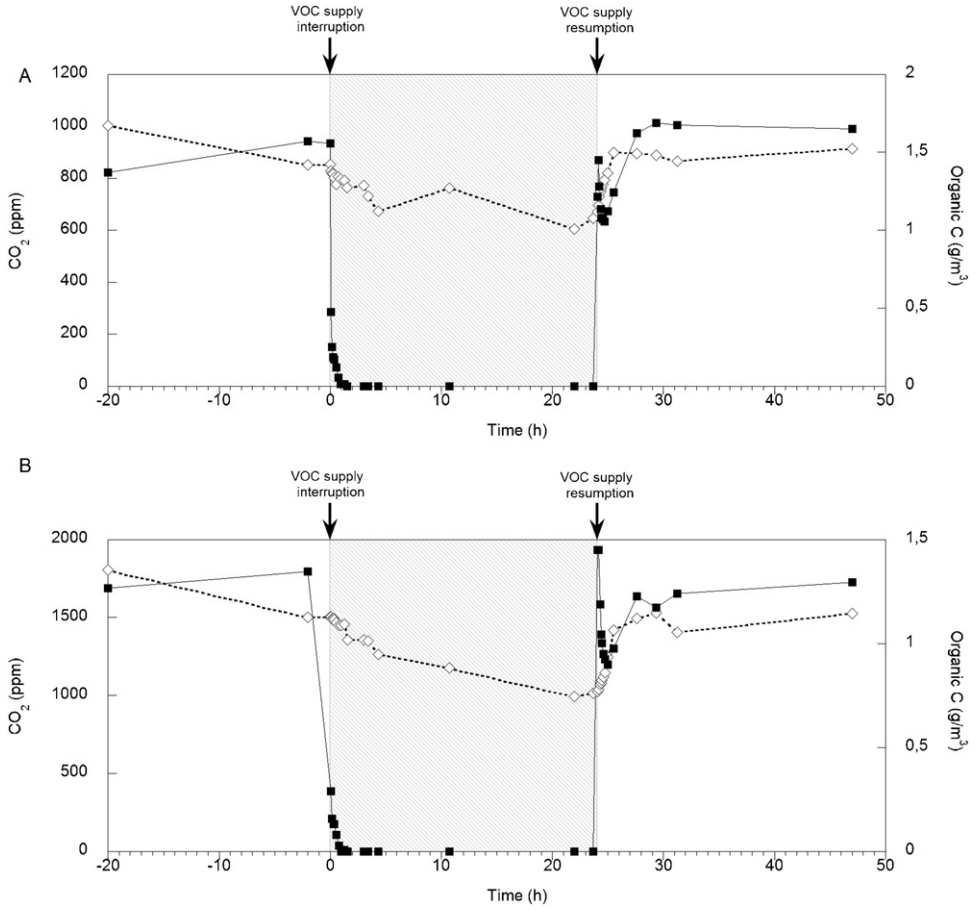

Fig. 3. Time course of the CO_2 concentration (◊) and organic C concentration (■) during the starvation experiment in the outlet of the fungal (A) and the bacterial biofilters (B).

pollutant uptake caused by the previous famine period. Both biofilters recovered steady REs and CO_2 production levels after 4 h. These results are in agreement with literature data where short recovery times were reported after starvation periods for both fungal and bacterial biofilters [7,13,27].

3.4. Metabolites identification

The identification of intermediate metabolites included the analysis of samples of the leachate and outlet gas condensate from both biofilters on day 47 and on day 6 of the combined bacterial–fungal operation. Two metabolites were identified by GC–MS with a match quality higher than 90%: Hexanal and 1-propanol. Despite that hexanal was detected in the outlet stream condensate of both biofilters, it was not present in the leachates, probably due to its higher volatility (Henry's law constant of $8.6 \times 10^{-3}\ C_g/C_l$) compared with that of hexanol (Henry's law constant $7.7 \times 10^{-4}\ C_g/C_l$), which was indeed detected both in the gas condensates and in the leachate of both biofilters [20]. The presence of hexanal was anticipated since hexanol biodegradation is mediated by the enzyme alcohol dehydrogenase (ADH), which oxidizes alcohols to aldehydes or ketones [15,28]. Surprinsingly 1-Propanol was detected in both the outlet condensates and leachates of both biofilters. This production of an alcohol from a more oxidized substrate such as propanal under aerobic conditions deserves further investigation. In this context, the production of biodegradation intermediates must be carefully assessed, even though they are in much smaller concentration that the inlet pollutants [15], as they might generate secondary pollution.

3.5. Fungal/bacterial coupled biofiltration

This configuration (bacterial → fungal reactors in series) was selected to avoid the carry-over of fungal spores and under the hypothesis that the most water soluble VOCs would be degraded in the first bacterial stage promoting the biodegradation of the hydrophobic VOCs by the fungal community. During the 16 days of stable operation of the two-stage bacterial-fungal biofilter the overall EC obtained ($38.4 \pm 8.4\ g\,C\,m^{-3}$ reactor h^{-1}) was slightly lower than the one obtained in bacterial biofiltration but significantly higher than the EC recorded for the fungal biofilter. The individual ECs of each biofilter under this configuration were half than those under single-stage operation due to the reduced EBRT in each individual biofilter (30 s instead of 60 s). Surprisingly, this reduction in the individual abatement performance of each stage was more significant in the bacterial biofilter (EC $20.1 \pm 5.9\ g\,C\,m^{-3}$ reactor h^{-1}, corresponding to a reduction in EC of 50.1%) than in the fungal biofilter (EC $18.9 \pm 7.9\ g\,C\,m^{-3}$ reactor h^{-1}, corresponding to a reduction in EC of 31.7%). The pressure drop in this two-stage biofilter doubled that of fungal biofiltration on day 60, which is consistent with the fact that gas flow was increased to maintain the same residence time (Table 1). On the other hand, a high and increasing VOC mineralization ratio (C produced as CO_2/C eliminated) was recorded, which finally became stable at ≈0.9. This sharp increase in the fungal mineralization ratio (from ≈46% during

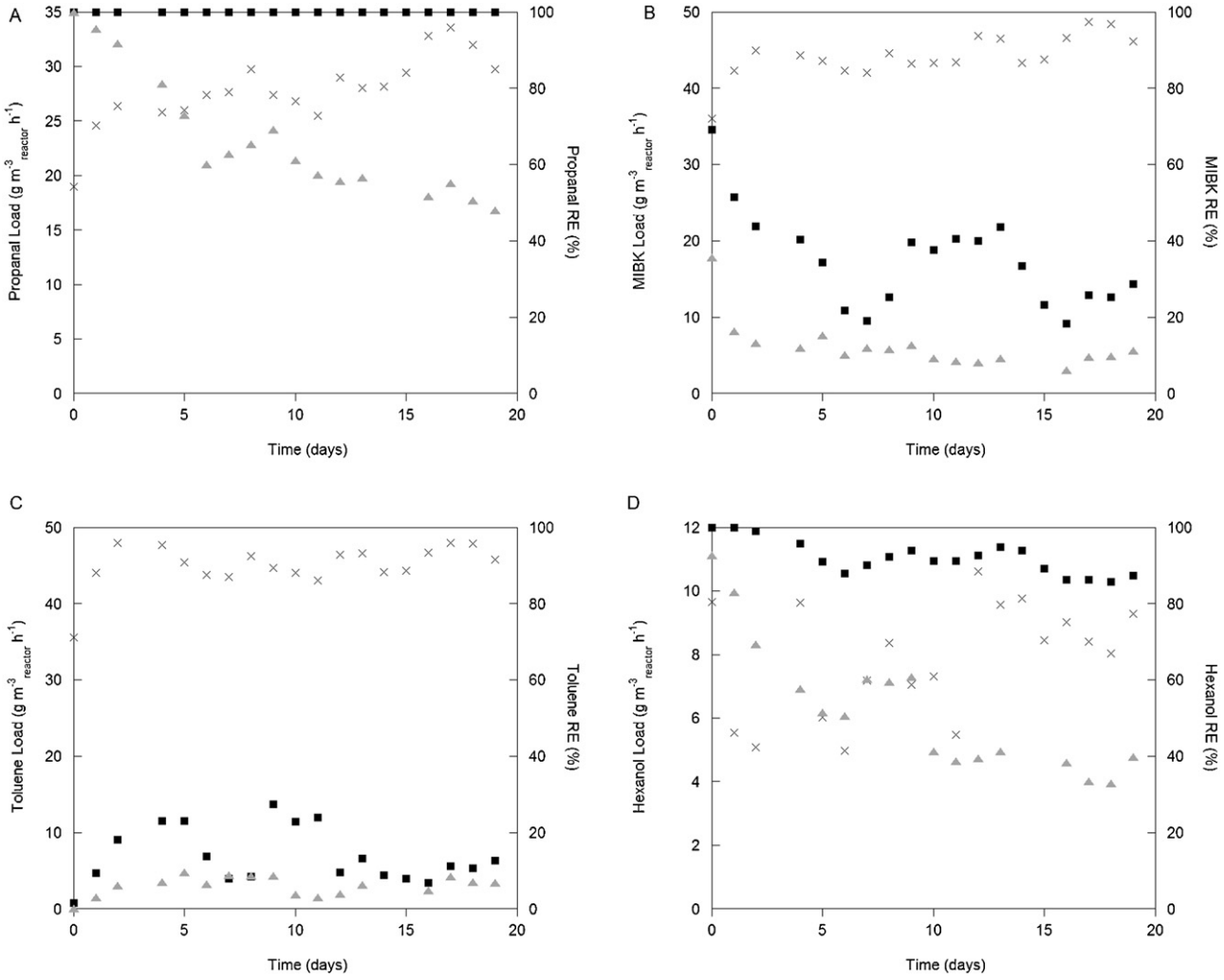

Fig. 4. Time course of the loading rate (×), bacterial stage RE (▲) and global RE (■) of propanal (A), MIBK (B), toluene (C) and hexanol (D) in the two-stage biofilter.

stable single operation to ≈97% when located after the bacterial stage) might be related to the mite infestation of the fungal biofilter. The partial mineralization ratios, (0.75 ± 0.40 and 0.97 ± 0.56 for the bacterial and fungal stages, respectively) supports the hypothesis of an increased CO_2 production from the mite-mediated biomass turnover.

The initial overall decreasing performance observed in the bacterial stage RE was attributed to the resumption of propanal supply to the system. Under steady state (days 5–19), propanal was removed by $57.7 \pm 6.0\%$ in the bacterial stage while the fungal biofilter operated as a polishing step to achieve a total RE of $100 \pm 0.0\%$ over the last 14 days of experimentation (Fig. 4 A). MIBK underwent low REs in the bacterial stage ($9.8 \pm 1.8\%$) and the fungal stage ($25.4 \pm 8.9\%$), with a total RE of $30.1 \pm 8.6\%$ (Fig. 4 B). The overall toluene RE remained low and fluctuating ($13.2 \pm 6.4\%$) (Fig. 4C) with an even biodegradation in both stages ($6.4 \pm 2.0\%$ in the bacterial stage and $7.8 \pm 5.6\%$ in the fungal stage). Both toluene and MIBK exhibited the fluctuating RE patterns already observed in the bacterial and fungal biofilters when operated separately, which again suggests the occurrence of a inhibitory metabolite accumulation. Hexanol was evenly eliminated in the bacterial stage ($44.7 \pm 9.9\%$) and in the fungal stage ($39.9 \pm 2.7\%$) with a total $90.1 \pm 3.1\%$ (Fig. 4 D). Therefore, the results here obtained ruled out the initial hypothesis of a complete removal of the hydrophilic VOC fraction in the bacterial biofilter followed by the removal of the most hydrophobic VOC in the fungal section.

3.6. Conclusions

This study constitutes, to the best of our knowledge, the first systematic evaluation of fungal and bacterial biofilters in terms of abatement capacity of a mixture of VOCs and pressure drop. Overall, bacterial biofiltration supported higher elimination capacities and mineralization ratios than its fungal counterpart. This observation can be explained partly by the fact that the bacterial biofilter developed a more diverse population, originated from the activated sludge, as compared to the fungal biofilter which was inoculated with an axenic culture, although the development of a secondary fungal population may not be ruled out. However, both biofilters showed an excellent robustness versus 24 h VOC starvation episodes. The steady state operation also showed a similar order in the biodegradation preference (propanal > hexanol > MIBK > toluene) with propanal partially inhibiting the biodegradation of the rest of compounds. When deprived from propanal, both biofilters were able consume the other VOCs in a larger extent as shown by the similar EC in the presence and absence of propanal. The two-stage bacterial/fungal biofilter provided high levels of VOCs mineralization. However, the results obtained did not validate the initial hypothesis of an enhanced VOC removal by combining a preferred removal of the hydrophilic VOC fraction in the bacterial biofilter with the removal of the most hydrophobic VOCs in the fungal section

Acknowledgements

This research was supported by the Spanish Ministry of Science and Innovation (RYC-2007-01667 and BES-2010-030994 contracts and projects CTQ2009-07601 and CONSOLIDER-CSD 2007-00055) and the Regional Government of Castilla y Leon (VA004A11-2). This project was partially financed by CONACYT.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2013.01.064.

References

[1] R. Lebrero, L. Bouchy, R. Stuetz, R. Muñoz, Odor assessment and management in wastewater treatment plants: a review, Crit. Rev. Environ. Sci. Technol. 41 (2011) 915–950.
[2] J.E. Burgess, S.A. Parsons, R.M. Stuetz, Developments in odour control and waste gas treatment biotechnology: a review, Biotechnol. Adv. 19 (2001) 35–63.
[3] N. Kraakman, J. Rocha-Rios, M. van Loosdrecht, Review of mass transfer aspects for biological gas treatment, Appl. Microbiol. Biotechnol. (2011) 1–14.
[4] U. Friedrich, K. Prior, K. Altendorf, A. Lipski, High bacterial diversity of a waste gas-degrading community in an industrial biofilter as shown by a 16S rDNA clone library, Environ. Microbiol. 4 (2002) 721–734.
[5] N. Khammar, L. Malhautier, V. Degrange, R. Lensi, J.J. Godon, J.L. Fanlo, Link between spatial structure of microbial communities and degradation of a complex mixture of volatile organic compounds in peat biofilters, J. Appl. Microbiol. 98 (2005) 476–490.
[6] T.K. Ralebitso-Senior, E. Senior, R. Di Felice, K. Jarvis, Waste gas biofiltration: advances and limitations of current approaches in microbiology, Environ. Sci. Technol. 46 (2012) 8542–8573.
[7] R. Lebrero, E. Rodríguez, M. Martin, P.A. García-Encina, R. Muñoz, H_2S and VOCs abatement robustness in biofilters and air diffusion bioreactors: a comparative study, Water Res. 44 (2010) 3905–3914.
[8] J.W. van Groenestijn, W.N. van Heininge, N.J. Kraakm, Biofilters based on the action of fungi, Water. Sci. Technol. 44 (2001) 227–232.
[9] S. Arriaga, S. Revah, Improving hexane removal by enhancing fungal development in a microbial consortium biofilter, Biotechnol. Bioeng. 90 (2005) 107–115.
[10] A. Vergara-Fernández, S. Hernández, S. Revah, Phenomenological model of fungal biofilters for the abatement of hydrophobic VOCs, Biotechnol. Bioeng. 101 (2008) 1182–1192.
[11] E.I. García-Peña, S. Hernández, E. Favela-Torres, R. Auria, S. Revah, Toluene biofiltration by the fungus *Scedosporium apiospermum* TB1, Biotechnol. Bioeng. 76 (2001) 61–69.
[12] S. Arriaga, S. Revah, Removal of *n*-hexane by *Fusarium solani* with a gas-phase biofilter, J. Ind. Microbiol. Biotechnol. 32 (2005) 548–553.
[13] Y. Jin, L. Guo, M.C. Veiga, C. Kennes, Fungal biofiltration of α-pinene: effects of temperature, relative humidity, and transient loads, Biotechnol. Bioeng. 96 (2007) 433–443.
[14] E.R. Rene, M.C. Veiga, C. Kennes, Biodegradation of gas-phase styrene using the fungus *Sporothrix variecibatus*: impact of pollutant load and transient operation, Chemosphere 79 (2010) 221–227.
[15] I. García-Peña, S. Hernández, R. Auria, S. Revah, Correlation of biological activity and reactor performance in biofiltration of toluene with the fungus *Paecilomyces variotii* CBS115145, Appl. Environ. Microbiol. 71 (2005) 4280–4285.
[16] J.W. van Groenestijn, J.X. Liu, Removal of alpha-pinene from gases using biofilters containing fungi, Atmos. Environ. 36 (2002) 5501–5508.
[17] A. Vergara-Fernández, S. Hernández, R. Muñoz, S. Revah, Influence of the inlet load, EBRT and mineral medium addition on spore emission by *Fusarium solani* in the fungal biofiltration of hydrophobic VOCs, J. Chem. Technol. Biotechnol. 87 (2012) 778–784.
[18] I. García-Peña, I. Ortiz, S. Hernandez, S. Revah, Biofiltration of BTEX by the fungus *Paecilomyces variotii*, Int. Biodeterior. Biodegrad. 62 (2008) 442–447.
[19] A. Aizpuru, L. Malhautier, J.C. Roux, J.L. Fanlo, Biofiltration of a mixture of volatile organic compounds on granular activated carbon, Biotechnol. Bioeng. 83 (2003) 479–488.
[20] R. Sander, Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, 1999, Version 3 http://www.henrys-law.org
[21] C. Kennes, E.R. Rene, M.C. Veiga, Bioprocesses for air pollution control, J. Chem. Technol. Biotechnol. 84 (2009) 1419–1436.
[22] G. Gallastegui, A. Barona, N. Rojo, L. Gurtubay, A. Elías, Comparative response of two organic biofilters treating ethylbenzene and toluene after prolonged exposure, Process Saf. Environ. Prot. (2011).
[23] L. Cabrol, L. Malhautier, F. Poly, X.L. Roux, A.-S. Lepeuple, J.-L. Fanlo, Resistance and resilience of removal efficiency and bacterial community structure of gas biofilters exposed to repeated shock loads, Bioresour. Technol. (2012).
[24] P.M. Santos, J.M. Blatny, I. Di Bartolo, S. Valla, E. Zennaro, Physiological analysis of the expression of the styrene degradation gene cluster in *Pseudomonas fluorescens* ST, Appl. Environ. Microbiol. 66 (2000) 1305–1310.
[25] L. Cabrol, L. Malhautier, Integrating microbial ecology in bioprocess understanding: the case of gas biofiltration, Appl. Microbiol. Biotechnol. 90 (2011) 837–849.
[26] J.R. Woertz, W.N. van Heiningen, M.H. van Eekert, N.J. Kraakman, K.A. Kinney, J.W. van Groenestijn, Dynamic bioreactor operation: effects of packing material and mite predation on toluene removal from off-gas, Appl. Microbiol. Biotechnol. 58 (2002) 690–694.
[27] W.M. Moe, B. Qi, Performance of a fungal biofilter treating gas-phase solvent mixtures during intermittent loading, Water Res. 38 (2004) 2259–2268.
[28] E. Bingham, B. Cohrssen, C.H. Powell, Patty's Toxicology, 5th ed., John Wiley & Sons, New York, 2001.