

Performance of peat biofilters treating ethyl acetate and toluene mixtures under non-steady-state conditions

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ABSTRACT

This paper presents the response of peat biofilters to loading changes corresponding to industrial practices such as overnight and weekend shutdowns, intermittent emission or inlet concentration peaks. Three laboratory-scale reactors fed with air contaminated with ethyl acetate, toluene or a 1:1 mixture of ethyl acetate and toluene were operated under $65 \text{ g m}^{-3} \text{ h}^{-1}$ inlet load and 60 s EBRT during 16 h/day, 5 days/week. Dynamic behavior after feed resumption after night and weekend closures showed a 1-2 h period of transient response to recover stable CO_2 production values. No increase in VOC emission was observed, except for biofilters treating toluene for which a transient peak in VOC emission during 4-8 h after weekend closures was detected. More stressful conditions such as intermittent emissions (2 h-on/ 2 h-off, 16 h/day, 5 days/week), or inlet concentration peaks (40-min, 50% increase) were successfully handled in the biofilter treating only ethyl acetate; but deterioration in the operation was observed in presence of toluene. The system performance after 15-days starvation period was fully recovered in less than 8 h of re-acclimation period. Living and dead cells monitoring results are also presented.

1 INTRODUCTION

Most of VOC gaseous emissions from chemical process are often generated, in practice, in transient conditions related to flux variations, and daily and weekly rotations in the production. Data indicate that short-term transient loadings within certain range of

concentration must not cause performance problems on biofiltration (Deshusses *et al.*, 1996), however, at some severe conditions, high contaminant emissions can be expected (Moe and Li, 2004). Research on characterization of the transient response of biofilters to remove VOCs is still scarce and adequate process monitoring and control of biofilter performance will require improved knowledge of transient loading response characteristics (Wright *et al.*, 2005).

By other side, new techniques to explore the microbiological aspects of the biofiltration have just begun to be applied, mainly due to the difficulty of making detailed observations (Steele *et al.*, 2005). In this sense, direct cell count by staining with fluorochromes that distinguish between living and dead bacteria reveals greater bacteria concentrations than the plate count technique, since culture methods exclude any organisms that are not able to grow on the culture media (Tresse *et al.*, 2003).

The purpose of the present research was to investigate the biofiltration of ethyl acetate, toluene and the mixture of both pollutants, taking into consideration the following objectives: (1) to evaluate the response of the biofilters to intermittent feeding conditions (16-h on/8-h off, 5 days/week), long-term starvation (2-weeks without VOC feeding), and pulse-step changes in concentration; (2) to evaluate the possible inhibition effect of ethyl acetate on toluene removal; and (3) to determine the dynamics of living and dead cells in the biofilters for better understanding the link between operational and ecological aspects of the biofiltration.

2 MATERIALS AND METHODS

2.1 BIOFILTER SYSTEM

The biodegradation was carried out in three laboratory-scale biofilters (total length of 97 cm and an internal diameter of 13.6 cm) treating air polluted with ethyl acetate, toluene or with a 1:1 mixture of both pollutants. The biofilters were equipped with five sampling ports to measure gas concentrations, located at 0 (inlet port), 25, 50, 75, and 95 (outlet port) cm of column length. Additional ports located at 20, 40, 60 and 80 cm were used for temperature measurement and to recover filter bed samples.

Peat (ProEco Ambiente, Spain) was used as filter material, and inoculation with an adapted culture from activated sludge was performed; details were described elsewhere (Álvarez-Hornos *et al.*, 2006). Compressed, filtered and dried air was passed through a humidifier to assure a relative humidity value of at least 90 %. The empty bed residence time (EBRT) was adjusted to 60 s by using mass flow controllers (Bronkhorst Hi-Tec, Netherlands). VOC feed was introduced into the air stream by using a syringe pump (New Era, infusion/withdraw NE 1000 model, USA) and then, the contaminated air was flowed downwards into the bed. The strategy adopted to control the moisture content in the biofilter bed was by feeding the air previously

humidified, as well as pouring on top of the biofilter 250-500 mL of a pH-buffered and nutrient solution (5.23 g/L K_2HPO_4 , 0.30 g/L KH_2PO_4 , 3.00 g/L NH_4Cl , pH = 8.00) each 2-3 days.

2.2 OPERATIONAL CONDITIONS

The biofilters were operated in parallel at $65 \text{ g m}^{-3} \text{ h}^{-1}$ of continuous IL (inlet load) for more than three months (phase 0) before starting intermittent loading experiments. Several phases were consecutively performed:

- Phase I: To simulate shift work of many industrial facilities, intermittent loading during 16 h/day, 5 days/week at identical instantaneous IL than in phase 0 was applied. Uncontaminated air during night and weekend closures was supplied.
- Phase II: To simulate intermittent pattern emission, 4 cycles of 2 h-on/2 h-off during 5 days/week were performed at an IL of $130 \text{ g m}^{-3} \text{ h}^{-1}$ during VOC feeding.
- Phase III: A long-term starvation period of 15 days without VOC loading, but with air flow through the biofilters, was applied.
- Phase IV: After time, intermittent loading similar to phase 1 was carried out to evaluate the re-acclimation of the biofilters under discontinuous operation.

In addition, shock loading experiments to study the dynamic response of the biofilters to inlet concentration peaks were carried out. Each biofilter was exposed on three consecutive days to 40-min step of a 50% inlet concentration higher than the regular feed.

2.3 ANALYTICAL TECHNIQUES

VOC concentration profiles were monitored daily by using a gas chromatograph (GC 8000 model, CE Instruments, Spain) equipped with a 0.86 mL automated gas valve injection system and a flame ionization detector. The chromatographic packed column was 10 % SP-1000 on 80/100 SUPELCOPORT, 10' (ID 1/8"). The gas carrier was helium ($35 \text{ cm}^{-3} \text{ min}^{-1}$) and the temperatures of the injection port, oven and detection port were 200, 60 and 250 °C, respectively. Response of the systems after feed resumption was evaluated, in terms of total VOC concentration, by using a total hydrocarbon analyzer (Nira Mercury 901 model, Spirax-Sarco, Spain). CO_2 concentrations in the five ports were measured by using a NDIR carbon dioxide analyzer (Gaswork NDIR model, Seda, Spain). The three equipments were calibrated by using standard gaseous mixtures supplied by Carbueros Metálicos, Spain.

Bacteria were enumerated by fluorescence microscopy using LIVE/DEAD® BacLight™ Bacterial Viability Kit (Invitrogen, USA), thus co-staining was performed

with SYTO 9 to define the number of living cells and with propidium iodine to define the dead ones. Samples were taken from the four sampling ports each 1-2 weeks. Microorganisms were dispersed from peat, stained and recovered onto membrane microfilters, as described in Álvarez-Hornos *et al.* (2007). Filters were mounted on microscope slides in mounting media (Invitrogen) and examined using an epifluorescence microscope (Nikon Eclipse E800, Japan) equipped with a blue excitation filter (B-2A; ex 450-490 nm, dm 505 nm, ba 520 nm) and a green excitation filter (G-2A; ex 510-560 nm, dm 575 nm, ba 590 nm). Living and dead cells were enumerated counting ten random microscopic fields three times, with an average standard deviation of 8.7% (maximum value of 37.3%).

3 RESULTS AND DISCUSSION

3.1 PERFORMANCE OF BIOFILTERS

The results of the biofilters monitoring are presented in Figure 1. For all biofilters, similar RE (removal efficiency) was achieved under intermittent loading than in continuous one, demonstrating the process capacity to handle shift work. However, the response of biofiltration process to shutdown periods depended on the pollutant and on the operational conditions. For pure ethyl acetate (Figure 1a), deterioration in global performance was not detected for overnight and weekend closures. For pure toluene, greater penetration into the bed was obtained after weekend closures (Figure 1b, days 6, 13, 20, 27, 34, 41). The presence of ethyl acetate resulted in a decrease of toluene RE (Figure 1c), especially high toluene penetration was observed after weekend closures (days 4, 11, 18).

Under 2 h-on/2 h-off cycling pattern (phase II), only ethyl acetate was successfully degraded, although the contaminant penetrated deeper into the filter bed, showing the adverse response of the biological activity as off-time period and instantaneous IL increased. For pure toluene, RE decreased to values around 70% – 75%, with outlet toluene concentrations between 500 and 650 mg m⁻³, then the test was stopped.

From the first day of the operation after 15 days of starvation (phase IV), RE in the three biofilters was restored to the values obtained in phase I at same feeding conditions. Biomass re-acclimation was shorter than 6 h, demonstrating the feasibility of the peat biofilters to work under prolonged cut-off. Cox and Deshusses (2002) have reported 10-24 h of re-acclimation for 2-9 days of starvation in a biotrickling filter treating toluene.

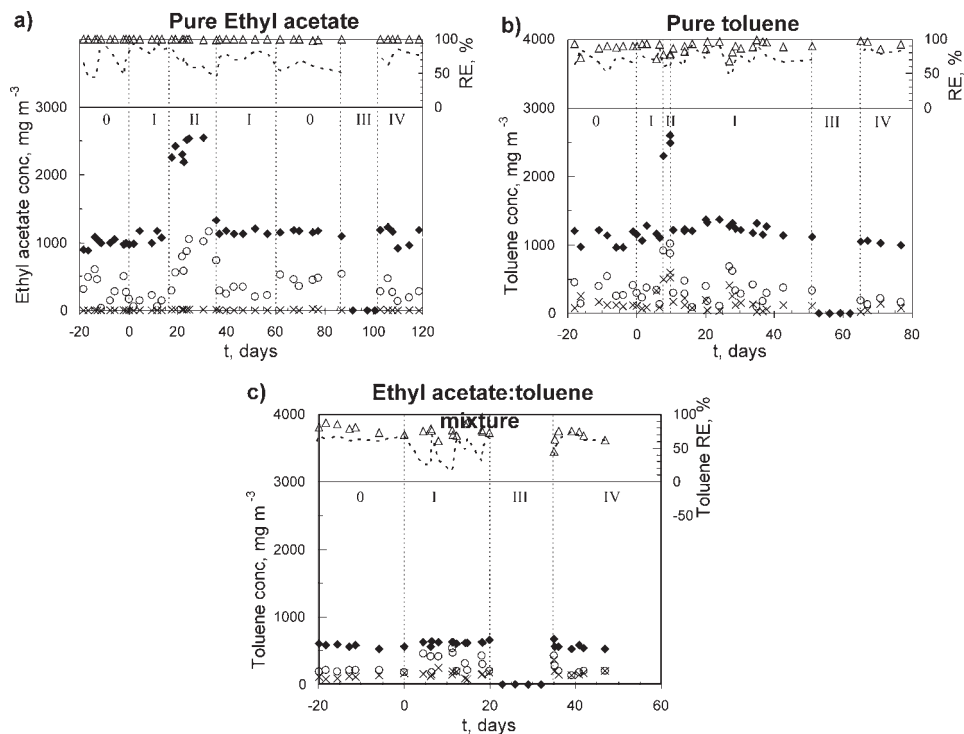


Figure 1. Monitoring biofilters performance. VOC concentration at the inlet (◆), first quarter of the biofilter (○) and outlet (x); overall RE (Δ) and RE at the first quarter of the biofilter (—).

3.2 EFFECT OF STARVATION ON BIOLOGICAL ACTIVITY

Determination of the carbon dioxide emissions after feed resumption is a fast respirometric measurement for the assessment of the effect of starvation periods on biological activity. Carbon dioxide production and outlet VOC concentration were monitored after night and weekend closures in phases I and II (Figure 2). For the mixture biofiltration, chromatographic analysis demonstrated that outlet emission was mainly composed of toluene ($95\% \pm 5\%$). Data from carbon dioxide production after overnight closures, plotted in Figures 2a, 2b and 2d showed similar tendency: after a lag of about 15-30 min, carbon dioxide production increased from values corresponding to endogenous metabolism to the stable total CO_2 production in less than 1-2 h, with the main increase observed from 30 min to 1 h period. For pure ethyl acetate, VOC emissions were always lower than 10 mgC m^{-3} (not shown). For feeds containing toluene (Figures 2c and 2e), no VOC emissions were observed in the first 30 min: toluene adsorption onto the biofilter might have occurred; and then a continuous increase during 1 h was observed until stationary values were reached.

For pure ethyl acetate, weekend closures presented similar CO_2 production pattern to overnight ones, although lag-time enlarged to 40-60 min. With toluene, greater time (4 - 6 h) was needed to fully restore the active metabolism, especially for the first weekend feed cut-off (day 6 for pure toluene, day 4 for the mixture). Microbial populations shifted in metabolism and more re-acclimation time to induce the toluene degradation pathway was needed. Besides, high toluene emissions with maximum concentrations corresponding to 30%-50% of toluene inlet concentration were produced in the first 2-4 h after feed resumption, and more than 4-8 h were needed to recover RE. Kim *et al.* (2005) reported a minimum time of 100-200 min to recover the RE of a biofilter fed with 0.2-2 g m^{-3} of toluene operated under 2 days/week starvation.

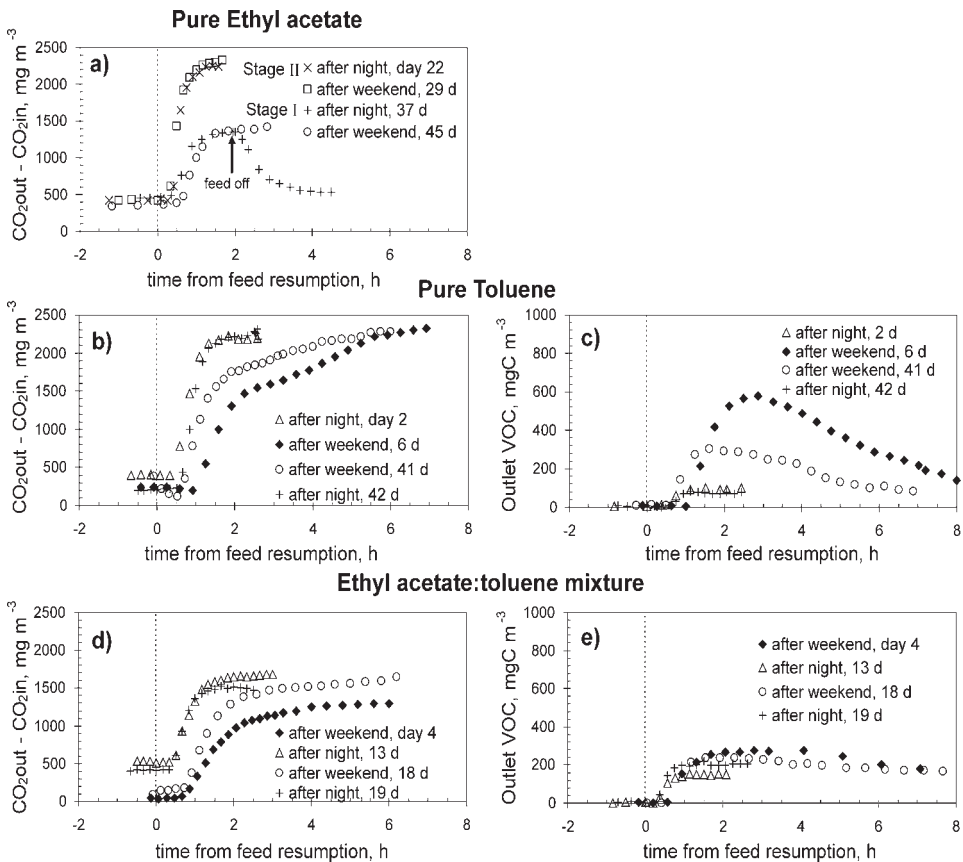


Figure 2. Immediate response of biofilters after night and weekend closure periods. (a) pure ethyl acetate, (b), (c) pure toluene; (d), (e) 1:1 ethyl acetate: toluene mixture.

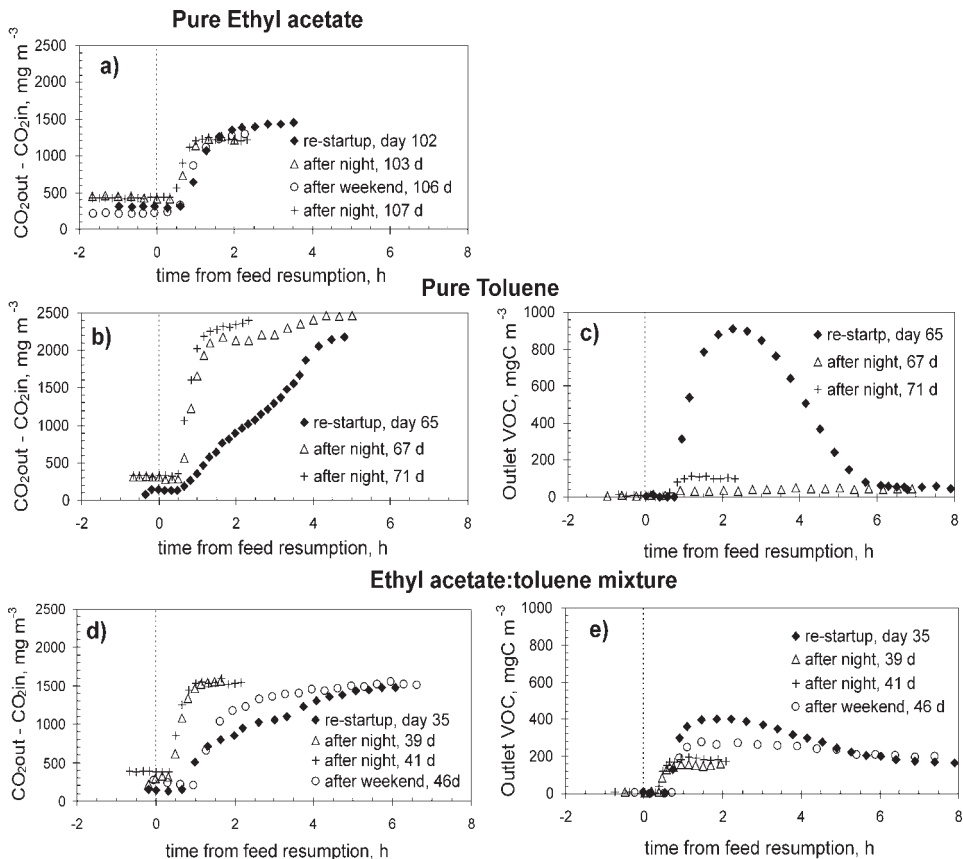


Figure 3. Immediate response of biofilters after 15-days feed cut-off, phase III. (a) pure ethyl acetate, (b), (c) pure toluene; (d), (e) 1:1 ethyl acetate: toluene mixture.

Results of monitoring the outlet CO_2 and total VOC concentration after the long-term starvation period of 15 days (phase IV) are presented in Figure 3. CO_2 production and outlet VOC patterns were similar to those observed previously at identical operational conditions (phase I, Figure 2) after night and weekend closures. This observation demonstrates that by using an organic support, with unpolluted air supply and moisture control, the environmental conditions and nutrients supply were enough to assure the bacterial population survival under endogenous metabolism for more than 15-days cut-off period. The evolution of CO_2 production immediately after re-startup after 15-days of starvation was almost identical to a weekend closure. However, greater toluene breakthroughs were observed, with maximum outlet concentrations of 92% and 82% of toluene inlet concentration for pure toluene and

the mixture, respectively. The period of 6 h to restore RE was not enlarged after 15 days of starvation in comparison with weekend closures. These data also indicate that the presence of ethyl acetate did not adversely affect the activation of the toluene degradation mechanisms after two weeks of starvation. These results are of great interest to demonstrate the feasibility of the biofiltration process to adequately respond to usual non-use periods related to holiday breaks at industrial sites.

3.3 DYNAMICS OF LIVING AND DEAD CELLS

Colonization dynamics monitoring in the four sections of the biofilters resulted in quite stable living bacteria density for the whole experimentation period, including the re-starting feed phase IV. Average living cells per gram of dry peat were 1.5×10^{10} (6.0×10^9 st. dev.) for the biofilter treating pure ethyl acetate, 1.3×10^{10} (4.5×10^9 st. dev.) for pure toluene, and 1.4×10^{10} (6.5×10^9 st. dev.) for the biofilter treating the mixture.

Results suggest that a healthy microbial population was maintained during the whole intermittent loading experiment. For pure toluene and the mixture, dead cell percentages maintained in high values around 76% from the beginning until phase III starting. In case of ethyl acetate, dead cell percentage suddenly increased from 34% to 75% when feed was changed from 16 h/d on to 2 h-on/2h-off cycles (phase II), and it remained quite constant until phase III starting.

After 15-d of starvation (phase IV), a reduction in total cell density was observed, yielding average dead cell percentages of about 41%, 64% and 41% for the biofilters treating pure ethyl acetate, toluene and the mixture, respectively. This observation suggests that living cells utilized dead ones as main carbon source in the long-term non-fed period. Results corroborated that non-use periods can be considered as a means of biomass control as previously reported by Kim *et al.* (2005) for low toluene loading biofiltration.

3.4 RESPONSE OF THE BIOFILTERS TO INLET CONCENTRATION PEAK

Here, transient response of biofilters to stepwise variation in inlet concentration, common problem that may occur in industrial sites, is examined. For each biofilter, inlet concentration was increased by 50% for 40-min on three consecutive days. Results from monitoring total VOC concentration at the first quarter (for pure ethyl acetate, no emission were detected at the outlet) or at the outlet (for pure toluene and for the mixture) and total CO₂ production are plotted in Figure 4. Chromatographic analysis indicated the absence of ethyl acetate at the outlet for the biofilter treating the mixture. For each biofilter, similar evolution was observed for the three days. The biofilter treating ethyl acetate (Figure 4a) was able to fully assimilate the transient peak working in 2 h-on/2 h-off cycles. Nevertheless, an increase in the pollutant breakthrough at the first quarter of the biofilter was rapidly developed and stabilized in less than 15-min

from the peak start. In case of toluene, biofilters were not able to assimilate the transient peak in smoother conditions (16 h/d-on stage). An increase in the pollutant emission was rapidly developed (< 10 -min) and average maximum emissions detected at the peak end were 307 mg-C m^{-3} (9% st. dev.) for pure toluene and 419 mg-C m^{-3} (14% st. dev.) for the mixture feed. For the three biofilters, return to the initial feed condition at 40-min caused a sudden recovery (< 10 -20-min) of the VOC concentration. In all cases, increases in CO_2 production were also observed. The 20-min gap between VOC outlet peak end and maximum CO_2 emissions indicated that microbial population needed some time to activate their metabolism under higher concentration of carbon source.

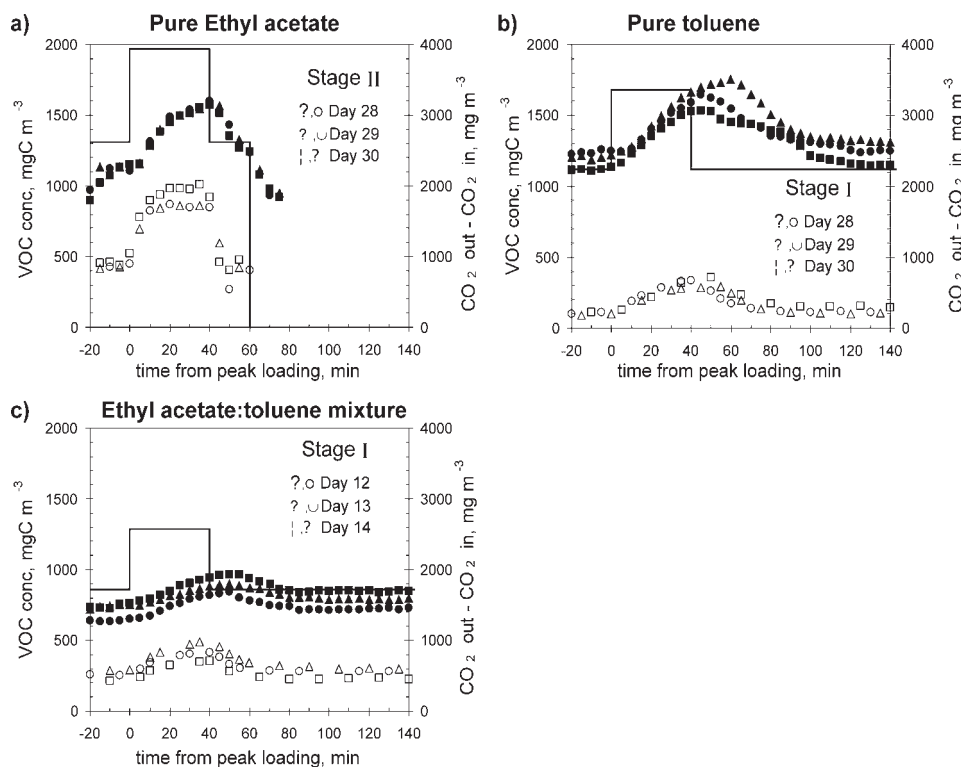


Figure 4. Response to inlet concentration peaks. Total VOC concentration at the inlet (—).

Solid symbols represent total CO_2 production.

Open symbols indicate total VOC concentration at first quarter for pure ethyl acetate (a), and at the outlet for toluene (b) and the mixture (c).

4 CONCLUSIONS

This study demonstrates the capacity of peat biofilters to handle intermittent loading conditions. Similar removal was achieved operating in a 16 h/day, 5 days/week regular feed mode (at $65 \text{ g m}^{-3}\text{h}^{-1}$ of instantaneous IL and 60 s of EBRT) than in continuous loading. The presence of ethyl acetate affected adversely to toluene RE, resulting in greater toluene penetration into the bed in comparison with pure toluene biofiltration. Some differences between toluene and ethyl acetate, more easily biodegradable compound, can be pointed out:

- Treating pure ethyl acetate it was possible to achieve low emissions even when more severe conditions (2-h on/2-h off cyclic loading during 16 h/d) were applied.
- When inlet concentration peaks (40-min, 50% increase) were supplied, the presence of toluene resulted in high VOC emissions; only the biofilter fed with pure ethyl acetate was able to maintain complete removal efficiency.
- For the three biofilters, night closure did not affect the RE, and CO_2 productions were restored in stable values in less than 1 - 2 h. But restart-up after weekend closures resulted in high toluene emission in the first 6 h, while VOC emission was not detected in case of pure ethyl acetate biofiltration.
- After 15-days of starvation, CO_2 production indicated the recovery of the active metabolism in less than 6 h with full restoration of the RE with toluene. In case of pure ethyl acetate, complete RE was obtained from the beginning, and the CO_2 production was restored in less than 2 h.
- For the three biofilters, living cell density remained quite stable for the whole experimentation period. Besides, after 15-days of starvation period, dead cell percentages decreased, especially for the biofilter treating pure ethyl acetate.

5 ACKNOWLEDGEMENTS

Financial support by Ministerio de Educación y Ciencia, Spain (research project CTM 2004-05714-C02-01/TECNO with FEDER funds) is acknowledged. F. Javier Álvarez-Hornos has a FPU grant from Ministerio de Educación y Ciencia, Spain.

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