Removal of a mixture of oxygenated VOCs in a biotrickling filter

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ABSTRACT

Laboratory scale-studies on the biodegradation of a 1:1:1 wt mixture of three oxygenated volatile organic compounds (VOCs), ethanol, ethyl acetate and methyl-ethyl ketone (MEK) in a biotrickling filter were carried out using two identically sized columns, filled with different polypropylene rings. The reactors were seeded with a two-month preconditioned culture from activated sludge. The performance of the biotrickling filters was examined for a continuous period of 4 months at VOC concentration from 125 mg-C/m^3 to 550 mg-C/m^3 and at gas flow rates of around 1.0 m^3/h, 2.0 m^3/h and 4.6 m^3/h, which correspond to gas empty bed residence times (EBRT) of 68 s, 33 s and 16 s, respectively. Similar performance was obtained for both supports. Intermittent flow rate of trickling liquid was shown as beneficial to improve the removal efficiency of the system. A stratification in the substrate consumption was observed from gas composition profiles, with MEK % in the emission greater than 78%. Continuous VOC feeding resulted in an excessive accumulation of biomass and high pressure drop was developed in less than 20-30 days of operation. Intermittent VOC loading with night and weekend feed cut-off periods passing dried air, but without water addition, was shown as a successful operational mode to control the biofilm thickness. In this case, operation at high inlet loads was extended for more than 50 days maintaining high removal efficiencies and low pressure drops.

1 INTRODUCTION

Biotrickling filters for air pollution control use a well-specified inorganic packing material and involves a liquid phase, which trickles through the bed. The liquid phase provides nutrients to the biofilm and allows for pH control, yielding a more stable operation in comparison with biofilters. These characteristics along with a larger air/liquid interfacial area lead to removal rates which are substantially higher than those obtained with conventional biofilters (Koutinas *et al*., 2005), implying potentially lower sizes and lower capital expenditure for industrial applications. These factors have caused a shift in interest from conventional biofilters to biotrickling filters in the recent years. A major disadvantage limiting its use for VOC removal is the clogging that occurs as a result of excessive microbial accumulation. Excessive biomass formation leads to progressive bed obstruction and is accompanied by an increase in pressure drop and channelling (Iliuta *et al*., 2005). To overcome this problem, the inert packing material can be cleaned by regular backwashing or by using chemicals.

The number of studies concerning VOC removal by biotrickling filters has increased in the past decade (Iranpour *et al*., 2005). However, few studies have been focused on treating mixtures of pollutants (Kim *et al*., 2005; Paca *et al*., 2006) and on intermittent operation (Cai *et al*., 2005; Cox and Deshusses, 2002). By other side, although the effect of biomass accumulation on pressure drop has been reported (Cox and Deshusses, 1999; Smith *et al*., 1998; Weber and Hartmans, 1996), the optimization of operational parameters to avoid this problem still needs further research.

The purpose of the present research was to investigate the removal of a mixture of three easy biodegradable oxygenated compounds: ethanol, ethyl acetate and methyl-ethyl ketone (MEK) by two lab-biotrickling filters filled with different inert supports, taking into consideration the following objectives: (1) to study the interactions among the degradation rates of the three compounds, (2) to evaluate the clogging problems under different operational conditions, (3) and to show the benefits of short-term starvation periods in clogging control at high VOC loadings.

2 MATERIALS AND METHODS

2.1 Biotrickling filter system

The experiments were performed using two identical laboratory-scale biotrickling filters, BTF1 and BTF2, constructed each of them of three cylindrical modules, with a total length of 120 cm and internal diameter of 14.4 cm. The packed bed contained four equidistant gas sampling ports and three equidistant bed sampling ports. Both reactors were filled with different polypropylene rings. The rings of reactor BTF1 had a nominal diameter of 40 mm and 97% of initial porosity. The reactor BTF2 was filled with Pall rings: first module was packed with 25 mm nominal diameter rings (initial porosity of 92%) and the other two modules were filled with 15 mm rings (initial porosity of 87%). The reactors were also provided with 20-cm of top and bottom spaces. The 1:1:1 wt mixture of ethanol, ethyl acetate, and MEK was introduced into the compressed, filtered and dried air by using a syringe pump (New Era, infusion/

withdraw NE 1000 model, USA). Contaminated air was introduced through the bottom of the column; flowrate was adjusted by using mass flow controllers (Bronkhorst Hi-Tec, Nederlands). The setup was completed with a 14-L recirculation tank. The recirculation solution, renewed every week, was fed into the reactor in a counter-current flow with respect to air flow by using a centrifugal pump at 2 - 4 L/min. The nutrient solution (composition in g L^{-1}: KH_2PO_4 5.8; K_2HPO_4 10.1; KNO_3 50.3; $MgSO_4 \cdot 7H_2O$ 1.9, Ca, Fe, Zn, Co, Mn, Mo, Ni and B at trace doses, pH = 7.0) was supplied once per day (on working days) into the recirculation tank. The volume of nutrient solution was adjusted depending on the inlet load applied to assure $N\text{-}NO_3$ concentrations greater than 10 mg L^{-1}.

Total concentration of VOC was measured by using a total hydrocarbon analyzer (Nira Mercury 901 model, Spirax-Sarco, Spain). The inlet and outlet gas streams were monitored daily and the intermediate ports were monitored once a week. The composition of the gas streams were periodically determined 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. Pressure drop was monitored daily when water was trickled through the beds. Soluble COD (Chemical oxygen demand), suspended solids and $N\text{-}NO_3$ concentrations along with conductivity and pH of the recirculation solution were also monitored daily. The void fraction at the first one-third of the beds was determined once a week. BTF performance was evaluated in terms of inlet load (IL), elimination capacity (EC) and removal efficiency (RE).

2.2 Operational conditions

The two parallel reactors were operated in three consecutive phases:

– Phase I (day 1 to 44): In this phase, continuous VOC feed was applied. After inoculation with a two-month preconditioned culture from activated sludge, the start-up was performed working at 33 g-C $m^{-3}h^{-1}$ of IL and 1.0 m^3h^{-1} of gas flow rate until high removal efficiency was reached. Five days later, the gas flow rate was increased to 2.0 m^3h^{-1} and two increasing inlet loads were applied: 33 and 63 g-C $m^{-3}h^{-1}$. Washing was applied as clogging control technique as follows: two-thirds of the BTF was filled with tap water, and then air was flown in pulses for 5 min.
– Phase II (day 45 to 79): After disassembling the reactors on day 44 to remove the excessive accumulation of biomass, a continuous IL of 36 g-C $m^{-3}h^{-1}$ was applied at a gas flow rate of 4.7 m^3h^{-1} to evaluate the total time until clogging occurred without washing. This strategy finally resulted in high pressure drops, so from day 79 to 89, two sequential starvation strategies were tested as possible procedures for clogging control: first, dried air without

VOC was supplied combined with water trickling for 15 minutes each 8 hours. Second, uncontaminated dried air was fed without water trickling.

– Phase III (days 89 to 140): Intermittent loading simulating shift work of many industrial facilities (16 h/day, 5 days/week) was applied. Uncontaminated dried air was supplied during night and weekend periods as a clogging control procedure. Water trickling was off during night closures. During weekends, water trickling was varied between 15 min/8 h to off depending on the biofilm thickness. Three increasing inlet loads were applied: 37, 63 and 141 g-C $m^{-3}h^{-1}$ at a constant gas flow rate of 4.7 m^3h^{-1}.

3 RESULTS AND DISCUSSION

3.1 Performance of biotrickling filters

The results of the monitoring of the biotrickling filters are presented in Figures 1 and 2 for BTF1 and BTF2, respectively. In part a), the total RE and inlet and outlet concentrations are plotted. In part b), the pressure drop and the void fraction at the first one-third of the reactors are presented. Performance parameters are resumed in Table 1 for the different phases.

Figures 1 and 2 show a similar performance of both biotrickling filters during the three phases. The start-up was successfully carried out, high RE was reached in 1-2 days for both reactors working at moderate conditions (IL of 33 g-C $m^{-3}h^{-1}$ and 68 s of EBRT). The decrease on RE observed on day 5 (Monday) was related to nitrogen exhaustion on the first weekend of operation. In phase I, operational conditions as nutrient dose or water trickling regime were regulated to improve the RE of the reactors, so this phase is characterized by some variability on RE. During the first two weeks of Phase I, high RE and low pressure drop was maintained in both BTFs. When inlet load was increased to 63 g-C $m^{-3}h^{-1}$, the continuous water trickling caused noticeable water retention, with partial flooding of the beds. Then, trickling regime was changed on day 22 from continuous to an intermittent mode (15 min/4 h). Besides, the intermittent water trickling was shown beneficial to improve the RE of the process in comparison with continuous trickling.

The pressure drop progressively increased due to the accumulation of biomass until 350-450 Pa m^{-1} were reached on day 22. By applying a specific washing cleaning to partially remove the excess biomass, pressure drop was restored in previous low values, but the systems were not able to keep on low pressure drop more over than 5-10 days. At the end of the phase I, pressure drop was in 443 Pa m^{-1} for BTF1 and 1384 Pa m^{-1} for BTF2. As pressure drop increased, void fraction decreased, reaching values lower than 60% at the first one-third of the column for pressure drop higher than 300 Pa m^{-1}.

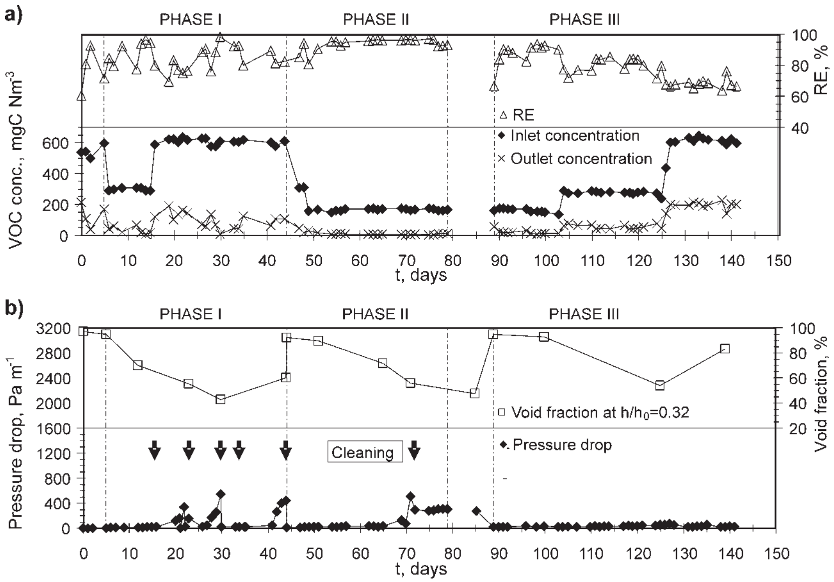

Figure 1. Monitoring the performance of biotrickling filter BTF1. a) VOC removal with time b) Evolution of the pressure drop and void fraction at the first one-third of the packed bed.

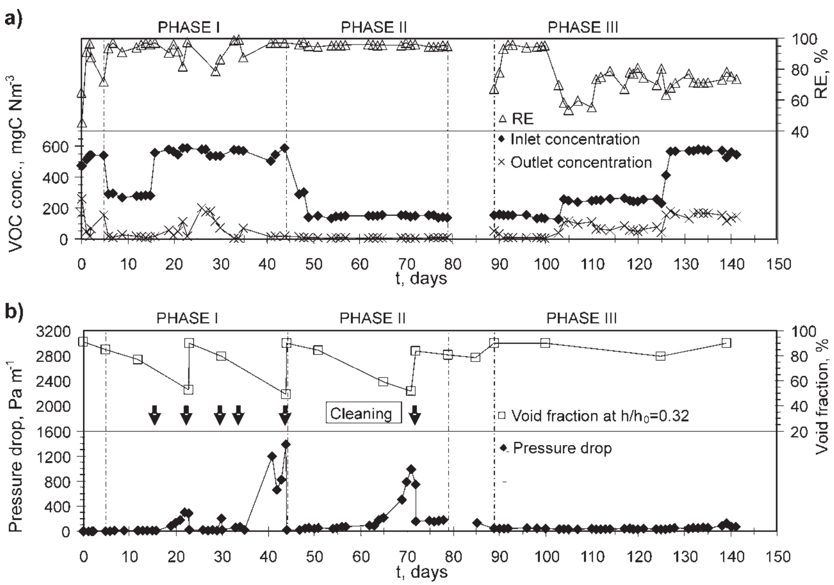

Figure 2. Monitoring the performance of biotrickling filter BTF2. a) VOC removal with time b) Evolution of the pressure drop and void fraction at the first one-third of the packed bed.

Table 1.
Performance parameters for both biotrickling filters on the different phases.

Days	EBRT, s		ILgC $m^{-3}h^{-1}$		ECgC $m^{-3}h^{-1}$		RE, %	
	BTF1	BTF2	BTF1	BTF2	BTF1	BTF2	BTF1	BTF2
Phase I								
5-15	33	35	32.3±1.4	29.2±0.9	28.1±2.8	27.8±6.5	86.7±6.7	95.1±2.4
15-44	33	35	62.9±3.8	58.4±2.1	52.3±4.7	53.6±5.1	83.2±7.3	91.7±7.1
Phase II								
48-79	16	15	36.4±5.1	33.4±4.8	34.2±5.2	31.9±4.6	93.7±4.0	95.5±0.8
Phase III*								
91-104	16	15	36.9±2.7	33.7±2.7	33.6±1.9	32.0±2.5	91.0±1.9	95.0±0.9
110-122	16	15	62.8±3.4	58.4±2.4	52.2±3.7	45.1±1.7	83.1±2.1	77.2±2.8
125-141	16	15	140.8±4.0	133.0±3.8	96.2±4.4	96.1±2.2	68.3±3.2	72.3±2.9

* Data corresponding to monday (after weekend closure) were not considered.

In sight of the difficulties to adequately control the clogging at an IL of 63 gC $m^{-3}h^{-1}$, the reactors were disassembled on day 44 to remove the excess biomass prior to start the Phase II. In Phase II, IL was decreased to 36 g-C $m^{-3}h^{-1}$ to evaluate the total time needed to experience clogging problems working at 16 s of EBRT without washing. A 15 min/8h water trickling program was applied in this stage. From day 48, uniform and stable operation with high RE (> 94%) was observed in both biotrickling filters, even when high pressure drops were reached. On day 72, washing was conducted for both reactors, being the removal of accumulated biomass more effective on BTF2 than in BTF1. The systems were kept on high RE for another week more, but the presence of thick biofilms would have derived in clogging problems. So, a new strategy for clogging control was adopted: uncontaminated dried air was fed from day 79 to day 85 to promote the biological stabilization of the biomass; water trickling was maintained in 15 min/8 h. On day 85, although pressure drop remained in low values, no benefits in void fraction were attained. Thus, a more severe strategy was tested; water trickling was suppressed in order to facilitate the dehydration of the biofilm. On day 89, thin biofilms were observed and measures of void fraction indicated a restoration to values close to the initial ones. This result showed that dehydration periods could be beneficial to control the clogging problem derived from biofilm development.

Considering this observation and taking into account that common industrial application usually involves non-use periods associated to shift work, an intermittent loading pattern was applied to the reactors in Phase III. During night and weekend non-fed periods, uncontaminated dried air was supplied to promote the partial dehydration of the biofilm. Three increasing inlet loads were applied at an EBRT of 16 s, and in all cases, stable operation was achieved, even for the higher IL. Water trickling was intermittently fed during 15 min/8 h for the IL of 37 g-C $m^{-3}h^{-1}$, and during 15 min/4 h for higher ILs. Average maximum ECs of 96.2 g-C $m^{-3}h^{-1}$ and 96.1 g-C $m^{-3}h^{-1}$ were reached at ILs of 141 g-C $m^{-3}h^{-1}$ and 133 g-C $m^{-3}h^{-1}$ for BTF1 and BTF2, respectively. The re-acclimation response after weekend closures indicated a nearly full recovery after feed resumption. Only data measured on monday mornings (days 96, 103, 110, 117, 124, 131, 138) showed a 5-10 % decrease on typical RE. Pressure drop was kept in low values for more than 50 days without further cleaning. These results demonstrate the feasibility of the process working at high loading and short EBRT conditions: the intermittent loading allows the application of short-term starvation combined with dehydration periods to control the biofilm thickness that prevents from clogging.

3.2 Compound abatement

This section deals with the evaluation of the efficiency of the process for the individual components. Results from Phase III, corresponding to operation under controlled pressure drop, are discussed. Similar general tendencies were observed for both biotrickling filters. Data for BTF1 are presented herein as an example. Figure 3 shows the removal efficiency for each pollutant, ethanol, ethyl acetate and MEK versus the total VOC concentration in the mixture feed for biotrickling filter BTF1 at an air flow rate of 4.7 m^3h^{-1} (EBRT = 16 s). Ethanol and ethyl acetate were degraded more

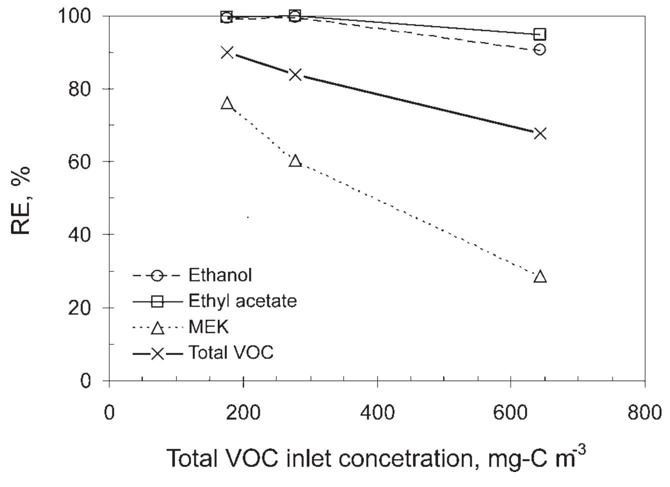

Figure 3. Removal efficiency of each pollutant in the biotrickling filter BTF1 as a function of the total inlet concentration of oxygenated VOCs at an EBRT = 16 s. Data obtained under intermittent loading conditions corresponding to Phase III.

efficiently than MEK. These compounds were fully removed for VOC concentration in the mixture feed up to 300 mg-C m^{-3}. For the highest inlet concentration tested, removal efficiencies slightly decreased to values of 91 and 95% for ethanol and ethyl acetate, respectively. Nevertheless, it was not possible to obtain so high MEK removal efficiencies in presence of ethyl acetate and ethanol, and MEK % in the emission remained always greater than 78%. For MEK, the removal efficiency varied as follows: from 175 to 644 mg-C m^{-3} of total VOC at the inlet, RE almost linearly decreased from 76% to 29%. Analyzing the total RE, it can be pointed out that biotrickling filter presented a competitive performance for treating the mixture of the three oxygenated compounds up to inlet concentrations as high as 300 mg-C m^{-3} by using an EBRT as short as 16 s.

The adverse effect of ethyl acetate and ethanol on the removal of MEK is shown in Figure 4, in which pollutant concentration profiles along the length of the biotrickling filter BTF1 are shown for the three total ILs applied in Phase III. Results show that at ILs of 40 and 64 g-C m^{-3}h^{-1}, ethanol and ethyl acetate were completely eliminated in the first two-thirds of the column, with most of removal (between 50 to 80%) taking place over the first one-third. For the IL of 148 g-C m^{-3}h^{-1}, a greater breakthrough along the bed was observed, with removal mainly taking place in the first two-thirds of the column. MEK profiles indicated a competition between substrates so that more easily biodegradable ethanol and ethyl acetate were used prior. For ILs of 40 and 64 g-C m^{-3}h^{-1}, MEK was used at a nearly constant rate throughout the total height. At an IL of 148 g-C m^{-3}h^{-1}, negligible MEK removal was observed in the first one-third of the column; MEK started to be used in the last zones of the column, where ethanol and ethyl acetate have been mostly degraded.

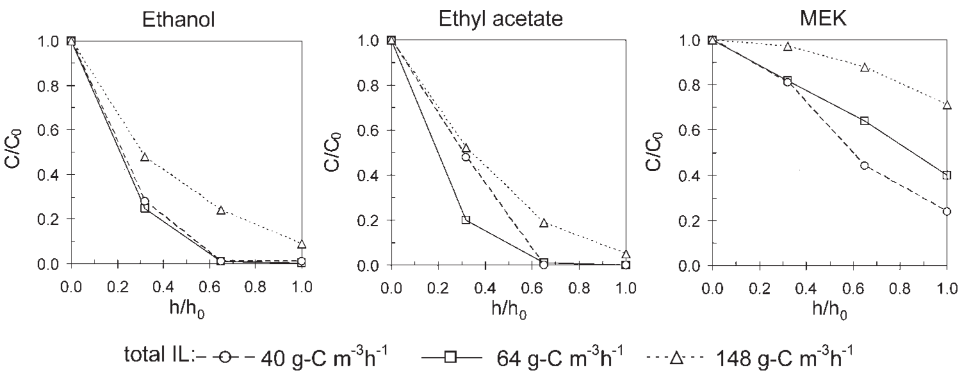

Figure 4. Pollutant concentration profiles along the length of biotrickling filter BTF1.
Data obtained under intermittent loading conditions corresponding to Phase III, EBRT = 16 s.

4 CONCLUSIONS

The removal of a mixture of three oxygenated VOCs, ethanol, ethyl acetate and MEK, in two biotrickling filters filled with different inert packing materials was investigated. No significant differences between both biotrickling filters were observed: similar removals and problems related to clogging were observed by using packing materials of different shape and initial void fraction.

Under continuous loading, both in a continuous or intermittent trickling of water, biofilm growth caused an increase in pressure drop resulting in clogging problems in less than 10-30 days of operation for total ILs of 37 and 63 g-C $m^{-3}h^{-1}$ and EBRTs of 16 and 33 s. Weekly washing could improve the short-term performance, but it was unable to assure a medium-term operation.

Intermittent loading operated 16 h/day and 5 days/week leads to short-term starvation periods that can be used to dehydrate the biofilm by combining inlet dried air with water trickling off. This strategy included intermittent water trickling and allowed achieving a stable operation at high loads and at short EBRT conditions with low pressure drop for more than 50 days; demonstrating its capability to adequately control the biofilm thickness and preventing clogging.

Ethyl acetate and ethanol presented similar removal profiles, they were used mainly in the first one-third of the column; but a greater stratification of the MEK degradation was observed. Competition among the pollutants defers the MEK consumption to the last zones of the column bed, where the easiest biodegradable compounds have been degraded.

5 ACKNOWLEDGEMENTS

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