Biotrickling filtration of isopropanol under intermittent loading conditions

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Abstract

This paper investigates the removal of isopropanol by gas phase biotrickling filtration. Two plastic packing materials, one structured and one random, have been evaluated in terms of oxygen mass transfer and isopropanol removal efficiency (RE). Oxygen mass transfer experiments were performed at gas velocities of 104 and 312 m h^{-1} and liquid velocities between 3 and 33 m h^{-1}. Both materials showed similar mass transfer coefficients up to liquid velocities of 15 m h^{-1}. At greater liquid velocities, the structured packing exhibited greater oxygen mass transfer coefficients. Biotrickling filtration experiments were carried out at inlet loads (IL) from 20 to 65 g C m^{-3} h^{-1} and empty bed residence times (EBRT) from 14 to 160 s. To simulate typical industrial emissions, intermittent isopropanol loading (16 h/day, 5 day/week) and intermittent spraying frequency (15 min/1.5 hours) were applied. Maximum elimination capacity (EC) of 51 g C m^{-3} h^{-1} has been obtained for the random packing (IL of 65 g C m^{-3} h^{-1}, EBRT of 50 s). The decrease in irrigation frequency to 15 min every 3 hours caused a decrease in the outlet emissions from 86 to 59 mg C Nm^{-3} (inlet of 500 mg C Nm^{-3}). The expansion of spraying to night and weekend periods promoted the degradation of the isopropanol accumulated in the water tank during the day, reaching effluent concentrations as low as 44 mg C Nm^{-3}. After a 7 week starvation period, the performance was recovered in less than 10 days, proving the robustness of the process.

Keywords

biotrickling filter, intermittent loading, isopropanol, oxygen mass transfer, volatile organic compounds

Introduction

Isopropanol is one of the main solvents used in chemical industries, and its manufacture worldwide exceeds $1x10^6$ tonnes per year. This results in a significant production of solvent organic wastes, including emissions to the atmosphere as volatile organic compounds (VOC). Since the abatement of

VOC is a factor in the protection of the environment and of public health in Europe [1], treatment technologies for VOC removal are required. When emissions are characterised by high flow rates and low VOC concentrations, biotreatments are suitable alternatives to conventional physicochemical technologies, and have been classified as best available technologies (BAT) [2] owing to their low operational costs and the minimisation of negative cross-media effects [3]. Compared to a conventional biofilter, a biotrickling filter (BTF) allows better control of the physicochemical parameters, offers a smaller footprint and higher removal rates. The BTF uses an inert packing material and involves the continuous or intermittent trickling of water. In this configuration, the biomass attaches to the media and develops a biofilm, thus the pollutant and the oxygen must be transferred from the gas phase to the trickling liquid and then to the biofilm, where the biodegradation takes place.

To enhance the performance of the BTF it is necessary to understand the rate limiting steps of the process. One of the most important limiting factors may be the mass transfer from gas to liquid and biofilm [4–6]. However, correlations commonly used for absorption in chemical processes do not correctly represent the phenomenon occurring in BTFs due to the different hydrodynamic conditions of chemical absorption. Absorption is marked by higher superficial velocities of the gas and liquid in comparison with BTF [7]. Treatment of hydrophilic compounds such as isopropanol, characterised by low Henry`s constants, could typically be limited by oxygen transference. Consequently, oxygen mass transfer should be systematically studied in these cases [7].

Despite being widely used in industrial and chemical processes, there are no previous studies on the removal of isopropanol by biotrickling filtration. Literature data about the removal of isopropanol by biofilters is also scarce compared with other solvents [8, 9]. These works have been performed under continuous and constant loading; the removal of isopropanol under oscillating and/or discontinuous emissions has not been previously reported. Most gaseous emissions from industrial processes are intermittently generated due to short-time shut off periods during the night and/or weekends. In fact, previous studies show that the operation of biofiltration under discontinuous VOC feeding regime can produce a degeneration of the system’s performance, although the literature in this field is still limited. Cox and Deshusses [10] reported that non-use periods cause a starvation condition on the microorganisms, which has been identified as one of factors that causes a reduction in pollutant removal.

These researchers observed that after 2 days of starvation, the endogenous respiration activity dropped by about 60 % and remained relatively constant thereafter.

The influence of long term starvation periods, without VOC feeding, also requires further study to advance the applicability of this technology. In our previous work, the reacclimation period, after 3 weeks without VOC feeding, was lower than 24 hours working at 60 s of EBRT in a BTF treating a mixture of ethanol, ethyl acetate and methyl-ethyl ketone (MEK), and operating under discontinuous loading [11].

The purpose of the present research was to investigated the removal of isopropanol using a BTF, taking into consideration the following objectives: (1) to determine the oxygen mass transfer coefficient of a structured and a random packing material, establishing a relationship between the mass transfer coefficient, the trickling flow rate and the specific surface area; (2) to compare the performance of the process, in terms of EC and RE, under isopropanol discontinuous loading conditions at several EBRT by using two BTFs operating in parallel, one filled with the structured and the other with the random material; (3) to evaluate the influence of spraying frequency on the RE, and (4) to evaluate the response of the BTFs to a long term starvation period representative of a holiday closure at an industrial site.

Materials and methods

Experimental set-up for the determination of oxygen mass transfer

The system consisted of a column of methacrylate (14.4 cm internal diameter, 80 cm height) and a recirculation tank (10 L of water volume). The schematic of the experimental set-up is shown in Fig. 1. The column was filled with two inert packing materials: a novel plastic cross-flow structured packing material (Odourpack, Pure Air Solution, The Netherlands) with 410 m^2 m^{-3} of specific surface area, and a random packing material (Refill-Tech, Italy) consisting of polypropylene rings with a nominal diameter of 5/8" and a specific surface area of 348 m^2 m^{-3}.The packing height was 20 cm for the structured packing and 40 cm for the rings. The air stream (compressed, filtered and dried) was introduced through the bottom of the columns, with the flow rate adjusted using a mass flow controller (Bronkhorst Hi-Tec, The Netherlands). The experiments were carried out at two air superficial velocities of 104 m h^{-1} and 312 m h^{-1}. The trickling water was recirculated using a centrifugal pump (HPR10/15, ITT, Great Britain) in

87 counter current mode with respect to the air flow rate, with a superficial velocity of the water between 3
88 and 33 m h^{-1}. The equipment is completed with a dissolved oxygen probe (Cellox® 325i, WTW,
89 Germany). An internal pump installed in the recirculation tank ensured the ideal mixing condition. The
90 experiments were carried out at room temperature (21.2 ± 0.7 ºC).
91
92 For the determination of k_La a dynamic method under inert conditions was used. The method consists of
93 measuring the increase of the oxygen concentration with time in a tank in which the oxygen has been
94 previously displaced by bubbling nitrogen gas. The experiment starts when the air blower and the
95 recirculation pump are switched on; oxygen is transferred from the air to the water in the packed column
96 causing an increase in the dissolved oxygen concentration in the recirculation tank. Under these
97 conditions, oxygen mass balances are as follows:
98 - In the packed column:

99 $$C_{out} = C^* - \frac{C^* - C}{\exp(\frac{L}{v} k_L a)}$$

100 (1)

101 where C_{out} is the predicted dissolved oxygen concentration at the bottom of the column, C is the predicted
102 dissolved oxygen concentration in the recirculation tank, C^* is the oxygen solubility and L and v are the
103 height of the column and the velocity of the trickling water, respectively.

104 - In the tank:

105 $$\frac{dC}{dt} = \frac{1}{\theta}\left(C_{out} - C\right) \quad (2)$$

106 where θ is the residence time in the tank.

107 The combination of Eqs (1) and (2) permits to obtain the variation of the predicted oxygen concentration
108 with time:

109 $$\frac{dC}{dt} = \frac{1}{\theta}\left(C^* - \left(\frac{C^* - C}{\exp(\frac{L}{v} k_L a)} - C\right)\right) \quad (3)$$

Due to the dynamics of the probe is not fast enough, it is necessary to take into account the response time constant of the probe, τ, defined as time that the probe achieves 63 % of the end value measured when the probe is subjected to a step input assay [12]. The response time of the probe was determined by transferring the oxygen probe from an ideal mixed tank in which the dissolved oxygen concentration was displaced by bubbling nitrogen gas to a second tank which is saturated with dissolved oxygen. It was assumed a first order dynamic according to Eq. (4) [13].

$$\frac{dC_m}{dt} = \frac{(C - C_m)}{\tau} \quad (4)$$

where C_m is the measured dissolved oxygen concentration in the recirculation tank by the oxygen probe.

The value of k_La of the packed column was calculated by minimising the sum of squares of the difference between the measured data recorded for dissolved oxygen concentration in the recirculation tank and the value obtained from the mathematical resolution of Eqs. (3) and (4).

Experimental set-up for the removal of isopropanol

The experiment was performed using two identical laboratory-scale BTFs operating in parallel, named BTF1 and BTF2. The experimental set-up is shown in Fig. 2. Each bioreactor was composed of three cylindrical methacrylate modules in series, with a total bed length of 100 cm and an internal diameter of 14.4 cm. BTF1 was filled with the structured material and BTF2 with the random packing, in each using a volume of 16.32 L. The bioreactors were also provided with 20 cm of top and bottom free spaces. The stream contaminated with isopropanol was introduced through the bottom of the column of the BTFs. A recirculation solution of 3 L, partially renewed every week, was fed into the bioreactor in counter-current mode with respect to the air flow using a centrifugal pump at 2.5-3 L min^{-1}. A nutrient solution buffered at pH 7 (21.65 g KNO_3 L^{-1}, 4.6 g $Na_3PO_4 \cdot 12H_2O$ L^{-1} and Ca, Fe, Zn, Co, Mn, Na, Ni, B, I, Se, Cr, Cu and vitamins at trace doses) was supplied to the recirculation tank using a peristaltic pump. The nutrient solution flow rate was set to maintain a supplied mass ratio of carbon and nitrogen (C/N) of 35, in order to assure that the nitrogen concentration in the recirculation solution was not limiting the biodegradation process. C/N mass ratios between 13 and 70 are suggested in the literature for the operation of bioreactors [14].

Influence of IL and EBRT on the removal of isopropanol

The operation of the bioreactors to determine the influence of IL and EBRT on the removal of isopropanol was structured in three phases (A, B, C) of a 2-fold step decrease in inlet concentration, phase A started with 1000 mg C Nm^{-3}. For each phase, several 1.8-fold IL step increases were carried out, resulting in EBRTs from 15 to 160 s. The design parameters of the experiments are summarised in Table 1. Intermittent feeding of VOC was programmed to simulate shift working conditions, which consisted in a regime of a period with VOC feeding of 16 hours per day (from 6:00 to 22:00 h) for 5 days at week, and night and weekend periods without VOC supply. The air flow rate was kept constant during both periods. Trickling water of 15 minutes every 1.5 hours was set during the VOC feeding period. During non-VOC feeding periods, the trickling water was stopped.

Influence of spraying frequency on the removal of isopropanol

The influence of the spraying frequency on the global performance of the system was evaluated by testing several patterns at an IL of 30 g C m^{-3} h^{-1} and EBRT of 60 s on the random packing material. Three frequency regimes were tested. Two of them were only applied during VOC feeding (16 hours per day, 5 days per week) with trickling water frequencies of 15 minutes every 1.5 hours or 15 minutes every 3 hours, spraying was stopped during the night and weekend periods. The expansion of spraying to the non-VOC feeding periods was tested by trickling 15 minutes every 3 hours over the whole day (24 hours per day, 7 days per week).

Influence of long-term starvation on the removal of isopropanol

The influence of a long period without VOC feeding on the performance of the BTF was evaluated by stopping the supply of isopropanol for a period of 7 weeks. During this time, the air flow rate was maintained at an EBRT of 60 s, and the water trickling was set to 15 minutes per day, to provide the minimum amount of nutrients and moisture that assures biomass viability. After that, the supply of isopropanol was restored using the same discontinuous VOC feeding mode (16 hours per day, 5 days per week) that was applied before the VOC interruption; IL of 35 g C m^{-3} h^{-1}, EBRT of 60 s and a trickling water frequency of 15 minutes every 4 hours was set.

Analytical methods

The oxygen concentration in the liquid was determined using a dissolved oxygen probe (Cellox® 325i, WTW, Germany). The concentration of isopropanol was measured using a total hydrocarbon analyzer (Nira Mercury 901, Spirax Sarco, Spain). The response factor of the total hydrocarbon analyzer was determined by gas chromatograph (model 7890, Agilent Technologies, EEUU). The CO_2 concentration was analysed using a nondispersive infrared carbon dioxide analyzer (GMP222, Vaisala, Finland). The inlet and outlet gas streams were monitored daily. The pressure drop was monitored daily (MP101, KIMO Instruments, Spain). To determine the quality of the recirculation solution, conductivity and pH (ph/Cond 340i, WTW, Germany), soluble chemical oxygen demand (COD), nitrate and suspended solids (SS) concentrations were measured prior to the weekly purge. Soluble COD and nitrate concentrations were measured using Merck Speqtroquant kits (Merck KGaA, Germany): 114540 (COD) and 114773 (nitrate). The SS concentrations were determined according to the Standard Methods for Examination of Water and Wastewaster [15].

Results and discussion

Determination of oxygen mass transfer coefficients

The determination of oxygen mass transfer coefficients was carried out for the two packing materials at several liquid velocities. The k_La coefficients were obtained using the least squares method in order to minimise the differences between the experimental data and the concentration of oxygen provided by the simple mathematical model established by Eqs. (3) and (4). The response time of the probe (τ) was determined earlier by means of a step input assay, resulting in a value of 19.4 ± 1.5 s. The effect of liquid velocity on mass transfer is shown in Fig. 3. The two packing materials presented a relationship between the liquid flow rate and the k_La values for a gas velocity of 104 m h^{-1} with similar values up to 15 m h^{-1}. For liquid velocities higher than this value, the structured material showed greater values of k_La. That difference cannot be explained by the slightly higher specific surface area of this material alone, it could be attributed to the different air and water flow paths in both materials. Selecting a liquid velocity of 10 m h^{-1} as representative of the operation of the BTFs in this study, a k_La approximately of 45 h^{-1} was obtained for both packing materials, without differences between them. The values obtained herein are of the same order of magnitude as those found by Kim and Deshusses [7] in previous papers. These authors reported a value of about 25 h^{-1} for liquid velocities around 10 m h^{-1} using 1" Pall rings (210 m^2 m^{-3}). These authors

showed that Onda's correlation overestimated the k_La values on biotrickling filtration by a factor of about 20 [16], indicating the need for determining oxygen mass transfer in the typical range of velocities of biotreatments.

The influence of gas velocity on the oxygen mass transfer coefficients has been determined with an additional test conducted at a gas velocity of 312 m h^{-1}. As an example, the results obtained for the structured packing material are shown in Fig. 4. As can be expected, these experiments demonstrate that k_La values were not significantly affected by gas velocities in the typical values of operation of BTFs.

Influence of inlet load and EBRT on the removal of isopropanol

The influence of inlet load on the removal of isopropanol in terms of EC and RE was evaluated. To simulate the emissions of industrial facilities, an intermittent VOC loading regime and a discontinuous trickling pattern was used. As an example, 24 hours of a typically daily evolution of VOC concentration in the outlet gas stream of the BTF2 is shown in Fig. 5. This figure represents the outlet emission pattern for two different stages where inlet concentrations of 1000 mg C Nm^{-3} (IL of 65 g C m^{-3} h^{-1}, stage A-III, Fig. 5a) and 500 mg C Nm^{-3} (IL of 35 mg C m^{-3}, stage B-II, Fig. 5b) were applied. As can be observed, the operating regime resulted in peaks of concentration coinciding with the irrigation of the bed (15 minutes every 1.5 hours). These peaks are related to the accumulation of the pollutant in the trickling water and subsequent desorption when trickling starts, resulting in outlet emission peaks. The comparison between both stages shows the influence of loading in the emission pattern. In the periods between trickling, a complete removal of pollutant was achieved for the lowest loading condition (Fig. 5b), while leakage of pollutant occurred for the highest load (Fig. 5a).

The monitoring of the quality of the trickling water was carried out twice per week for the whole experimental period. Average values along with the standard deviation are shown in Table 2. As shown in Table 2, the pH and conductivity were kept in normal values for the development of the biological process during the whole period. Nitrate in the water tank was kept above 10 mg N L^{-1} assuring that nutrients were not limiting the bioprocess. Soluble COD values ranged between 700–1800 mg COD L^{-1} depending on the loading conditions. The operational protocols regarding the quality of the trickling

219 water included a weekly purge of 1.5 L of water. In all cases, solvent removal with the purge represents
220 less than 5 % of the total amount of fed isopropanol during the week. In consequence, the organic carbon
221 in the purge was considered negligible for evaluation of the BTF performance in terms of inlet load (IL),
222 elimination capacity (EC) and removal efficiency (RE). About suspended solids, concentrations higher
223 than 500 mg L^{-1} were only observed since month 3, indicating that significant detachment of solids from
224 the packing materials started as the biofilm thickened. Average values of the suspended solids
225 concentration from day 90 until the end of the experimentation period resulted in 3151 mg L^{-1} and 1022
226 mg L^{-1} for BTF1 and BTF2, respectively. The higher suspended solid concentrations in BTF1 than in
227 BTF2 can be associated with the capability of the structured packing material to drag the biomass, in
228 comparison with the random packing where biomass is detached with greater difficulty. In both
229 bioreactors, the pressure drop was kept below 48 Pa m^{-1}, indicating that non excessive accumulation of
230 biomass occurred. The accumulation of acetone as an intermediate product was not observed.

231

232 To quantify of the outlet concentration of VOC, the most unfavourable conditions were selected. So, the
233 average values of the previous 7 hours during VOC feeding (from 15:00 to 22:00 h: last five spraying
234 cycles) was used. The performance of BTF1 and BTF2 is shown in Fig. 6a and Fig. 6b, respectively. A
235 similar evolution of both BTFs during the whole experiment was observed. The start-up was carried out
236 using activated sludge from the secondary clarifier of the municipal wastewater treatment plant of Carlet
237 (Spain). In order to simulate the procedure of the industrial BTFs, the inoculum was not previously
238 adapted to degrade isopropanol. The systems were started by setting an EBRT of 160 s for BTF1 and 152
239 s for BTF2 and an inlet concentration of 1000 mg C Nm^{-3} (phase A-I , day 0–48). After 4–6 days of
240 operation, REs of 70 % were obtained. After that the performance was stable, with REs around 80 % for
241 both BTFs. On day 49 (phase A-II) and on day 70 (phase A-III) the EBRT was consecutively decreased to
242 90 and 50 s, increasing the IL to 35 and 65 g C m^{-3} h^{-1}, respectively. During these stages, both BTFs
243 presented similar variability in their performance with REs ranging between 60 and 85 %. In phase B, an
244 inlet concentration of 500 mg C Nm^{-3} was set. REs greater than 90 % were achieved by applying ILs of
245 18 (phases B-I, days 91–97) and 33 g C m^{-3} h^{-1} (phase B-II, days 98–104). In phase B-III (days 105–125),
246 with an IL of 64 g C m^{-3} h^{-1}, the REs significantly decreased to 60–70 %. Finally, the inlet concentration
247 applied in phase C was 250 mg C Nm^{-3}. Working with an IL of 37 g C m^{-3} h^{-1} for BTF1, and 39 g C m^{-3} h^{-}

^{1} for BTF2 (days 126–132), high REs with values around 80 % for BTF1 and 88 % for BTF2, were observed. When the IL was increased to 65 g C m^{-3} h^{-1} (days 133–163), the performance of the BTFs decreased to reach a RE of 49 % for BTF1 and 60 % for BTF2, coinciding with the minimum EBRT applied (14 s).

The elimination capacity versus the inlet load is presented in Fig. 7 for the different EBRTs (BTF1 in Fig. 7a, BTF2 in Fig. 7b). Both BTF performed near complete degradation up to a critical IL of 30 g C m^{-3} h^{-1} for all tested inlet concentrations (EBRT>25s). Maximum ECs of 44.7 ± 5.3 g C m^{-3} h^{-1} and 50.8 ± 3.4 g C m^{-3} h^{-1} were obtained for BTF1 and BTF2 respectively (IL of 65 g C $m^{-3}$$h^{-1}$ and EBRT of 50 s).

No data related to the biodegradation of isopropanol under intermittent loading conditions has previously been published in the literature. Previous studies on the removal of isopropanol under continuous loading conditions are also scarce, and correspond with biofilters and trickled bed biofilters. Chang and Lu [8] found ECs between 45–89 g C m^{-3} h^{-1} for isopropanol loadings of 50–90 g C m^{-3} h^{-1} with EBRT of 20–30 s. Krailas et al. [9] reported a maximum isopropanol elimination capacity of 276 g m^{-3} h^{-1} (equivalent to 165 g C m^{-3} h^{-1}) and an acetone production rate of 56 g m^{-3} h^{-1} (equivalent to 35 g C m^{-3} h^{-1}) at an inlet load of 342 g m^{-3} h^{-1} (equivalent to 204 g C m^{-3} h^{-1}) using a biofilter. As can be seen, data reported in the present study show lower values of EC than those from the literature, due to the discontinuous operation used to mimic an industrial pattern. Results can also be compared with the removal of other hydrophilic compounds by biotrickling filtration, such ethanol. Working under continuous loading conditions, Cox et al. [17] found a critical IL of 70 g ethanol m^{-3} h^{-1} (equivalent to 37 g C m^{-3} h^{-1}) at an EBRT of 57 s, and Morotti et al. [18] determined a maximum EC of 46 g ethanol m^{-3} h^{-1} (equivalent to 24 g C m^{-3} h^{-1}) using an EBRT of 66 s and an inlet concentration of 1100 mg ethanol m^{-3}. Working under intermittent loading conditions, there are limited studies with BTF. In our previous work [19], a maximum EC of 48.5 g C m^{-3} h^{-1} was obtained with an IL of 70.5 g C m^{-3} h^{-1} and an EBRT of 40 s treating a mixture 1:1 of ethyl acetate and ethanol working with fluctuating conditions for 12 hours per day, 5 days at week using 1” polypropylene rings as the packing material. Thus, the data presented in the present work is comparable with those previously reported for the fluctuating conditions of other oxygenated solvents, showing the capability of the system to adapt itself to the typical operation of industrial facilities characterised by discontinuous VOC emissions.

The variation in the rate of carbon dioxide production with its elimination capacity is shown in Fig. 8a and Fig. 8b for BTF1 and BTF2, respectively. No significant differences were obtained between the bioreactors. An average yield of carbon dioxide of 0.25 ± 0.09 and 0.29 ± 0.09 g C CO_2 produced per g C degraded for BTF1 and BTF2 was obtained during the entire experiment, respectively. This value is similar to the data in the literature on treating oxygenated compounds. Sempere et al. [11] obtained an average CO_2 yield coefficient between 0.18 and 0.40 g C CO_2 produced per g C degraded treating a mixture of ethanol, ethyl acetate and methyl-ethyl ketone. Other researchers reported carbon mineralisation between 17 % [18] and 46 % [17] treating ethanol.

Influence of spraying frequency on the removal of isopropanol

As discussed previously, the discontinuous regime of the spraying of the bed resulted in emissions of isopropanol during irrigation, increasing the average outlet concentrations in the emission. A minimum irrigation is required to supply the nutrients, but, due to the high solubility of non-degraded isopropanol in water, the accumulation in the trickling liquid caused a fugitive emission that can be minimised, optimising the frequency of the spraying. The effect of this variable on the average outlet concentration was evaluated for the random packing material. Three regimes of spraying were applied at IL of 32 g C m^{-3} h^{-1} and EBRT of 60 s. Figs. 9a and 9b show the results of spraying 15 minutes every 1.5 hours and every 3 hours, respectively, only during the VOC feeding period (16 hours per day). Fig. 9c corresponds to a continuous trickling of 15 minutes every 3 hours over a 24 hours period, including the period without VOC.

From Figs. 9a and 9b it can be observed that by decreasing the spraying frequency per day it was possible to reduce the average daily outlet concentration from 86 to 59 mg C Nm^{-3} during the VOC feeding period. This decrease in the average daily outlet concentration is related to the fewer peaks of the spraying pattern of 15 minutes every 3 hours. The expansion of spraying at nights (Fig. 9c) caused a decrease in the average outlet emission from 59 to 44 mg C Nm^{-3} during the isopropanol feeding period. Spraying during non VOC feeding periods facilitated the VOC transfer to the biofilm and thus enhanced the degradation of the accumulated isopropanol in the water tank. Therefore the transfer from water to the air during

spraying decreases. These results indicated that for the removal of hydrophilic compounds, the spraying frequency is a critical parameter to achieve low emissions under discontinuous and oscillating patterns.

Influence of long term starvation on the removal of isopropanol

The BTFs were submitted to a starvation period to simulate a holiday industrial closure, in order to evaluate their response after restoring VOC feeding. During the long-term starvation, the air flow rate was maintained at an EBRT of 60 s, and water trickling was set to 15 minutes per day to assure biomass viability conditions. The BTFs were kept under these conditions for up to 7 weeks. The VOC feeding was restored using the same intermittent pattern of 16 hours per day that was applied before the VOC interruption. An IL of around 35 g C m^{-3} h^{-1}, EBRT of 60 s and a trickling water of 15 minutes every 4 hours was set. The monitoring of the inlet and outlet VOC concentrations of BTF1 and BTF2 is presented in Fig. 10a and Fig. 10b, respectively, once the VOC feeding was restored. As can be observed, REs of 80 % were obtained 5 days after the re-start up for both BTFs. After 10 days of operation, both BTFs achieved REs of 90 %, similar values to those obtained in phase B-II, indicating that the performance of the two bioreactors was fully recovered. These results show that the bacterial population can survive in endogenous metabolism for more than 7 weeks if proper adequate operational conditions are adjusted. Zhang and Bishop [20] suggested that extracellular polymeric substances can be a substrate during starving periods. Shorter starvation periods have also been tested on the degradation of other compounds in BTFs. Sempere et al. [11] reported on the successful reacclimation of a BTF degrading a mixture of oxygenated compounds after a 3 week starvation period. Cox and Deshusses [10] found a great reactivation of toluene-degrading BTFs after periods of 2 to 9 days without VOC feeding. The long starvation period tested in this study is of interest due to the fact it has never previously been applied in biotrickling filtration. It demonstrates the sturdiness of the biofiltration techniques to adapt to conditions found in industrial facilities, avoiding the necessity for system re-inoculation with the subsequent saving of costs.

Conclusions

The removal of isopropanol in two biotrickling filters with two packing material of similar specific surface area, one structured and one random, was investigated. Oxygen mass transfer coefficients were determined, showing similar values for liquid velocities up to 15 m h^{-1} at gas velocities of 104 and 312 m

h^{-1}. At higher liquid velocities, the structured packing material showed a greater mass transfer coefficient attributed to the different air and water flow paths in both materials. Biotrickling filtration has been shown as an effective technology for the removal of isopropanol in waste gases under intermittent loading conditions (16 hours per day, 5 days per week), typical of industrial sites with night and weekend shut-offs. Stable performance has been obtained with complete removal up to an inlet load of 30 g C m^{-3} h^{-1}. At high loads, the random packing material showed a slightly higher removal capacity. Due to the low Henry coefficient of isopropanol, it tends to accumulate in the water tank, causing a peak in the outlet emission during intermittent spraying. Thus, this fact indicates that the frequency of irrigation is a crucial parameter to achieve low emissions under intermittent loading of highly soluble compounds. Outlet emissions were reduced by half by decreasing the spraying frequency during isopropanol feeding, and expanding the irrigation to nights and weekends. This strategy allows the minimisation of peak emissions from liquid-mass transfer during isopropanol feeding periods, and promotes the biodegradation of isopropanol accumulated in water during non feeding periods. A fast re-start up after a 7 week starvation period, one of the longest reported, corroborated that biotrickling filtration of soluble compounds under intermittent loading is a robust technology for industrial applications.

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References

1. Council Directive 2010/75/EU of 24 November 2010 on industrial emissions (integrated pollution prevention and control). 17.12.2010. Official Journal of European Union

2. European Commission (2003) IPPC reference document on best available techniques in common waste water and waste gas treatment/management systems in the chemical sector. Sevilla

360 3. Devinny JS, Deshusses MA, Webster TS (1999) Biofiltration for air pollution control. CRC-Lewis
361 Publishers, Boca Raton

362 4. Popat SC, Deshusses MA (2010) Analysis of the rate-limiting step of an anaerobic biotrickling filter
363 removing TCE vapors. Process Biochem 45:549-555

364 5. Kirchner K, Wagner S, Rehm HJ (1992) Exhaust-gas purification using biocatalysts (fixed bacteria
365 monocultures) - The influence of biofilm diffusion rate (O_2) on the overall reaction-rate. Appl Microbiol
366 Biotechnol 37:277-279

367 6. Barton JW, Davison BH, Klasson KT, Gable CC (1999) Estimation of mass transfer and kinetics in
368 operating trickle-bed bioreactors for removal of VOCS. Environ Prog 18:87-92

369 7. Kim S, Deshusses MA (2008) Determination of mass transfer coefficients for packing materials used in
370 biofilters and biotrickling filters for air pollution control. 1. Experimental results. Chem Eng Sci 63:841-
371 855

372 8. Chang KS, Lu CS (2003) Biofiltration of isopropyl alcohol by a trickle-bed air biofilter.
373 Biodegradation 14:9-18

374 9. Krailas S, Suppalak T, Meeyoo V (2004) Macrokinetic determination of isopropanol removal using a
375 downward flow biofilter. Songklanakarin J Sci Technol 26:55-64

376 10. Cox HHJ, Deshusses MA (2002) Effect of starvation on the performance and re-acclimation of
377 biotrickling filters for air pollution control. Environ Sci Technol 36:3069-3073

378 11. Sempere F, Gabaldón C, Martínez-Soria V, Marzal P, Penya-Roja JM, Alvarez-Hornos FJ (2008)
379 Performance evaluation of a biotrickling filter treating a mixture of oxygenated VOCs during intermittent
380 loading. Chemosphere 73:1533-1539

381 12. Van't Riet K (1979) Review of measuring methods and nonviscous gas-liquid mass transfer in stirred
382 vessels. Ind Eng Chem Process Des Dev 18:357-364

13. Weiland P, Onken U (1981) Fluid dynamics and mass transfer in an airlift fermenter with external loop. Ger Chem Eng 4:42-50

14. Kennes C, Rene ER, Veiga MC (2009) Bioprocesses for air pollution control. J Chem Tech Biotechnol 84:1419-1436

15. Clesceri LS, Greenberg AE, Eaton AD (1998) Standard methods for the examination of water and wastewater. American Public Health Association, American Water Works Association and Water Environment Federation, Washington

16. Kim S, Deshusses MA (2008) Determination of mass transfer coefficients for packing materials used in biofilters and biotrickling filters for air pollution control - 2: Development of mass transfer coefficients correlations. Chem Eng Sci 63:856-861

17. Cox HHJ, Sexton T, Shareefdeen ZM, Deshusses MA (2001) Thermophilic biotrickling filtration of ethanol vapors. Environ Sci Technol 35:2612-2619

18. Morotti K, Ramirez AA, Jones JP, Heitz M (2011) Analysis and comparison of biotreatment of air polluted with ethanol using biofiltration and biotrickling filtration. Environ Technol 33:1967-1973

19. Sempere F, Gabaldón C, Martínez-Soria V, Penya-Roja JM, Álvarez-Hornos FJ (2009) Evaluation of a combined activated carbon prefilter and biotrickling filter system treating variable ethanol and ethyl acetate gaseous emissions. Eng Life Sci 9:317-323

20. Zhang XQ, Bishop PL (2003) Biodegradability of biofilm extracellular polymeric substances. Chemosphere 50:63-69

404 **Tables**

405 **Table 1** Experimental plan for the removal of isopropanol under intermittent loading conditions

		Days	C_{in} (mg C Nm^{-3})	IL (g C m^{-3} h^{-1})	EBRT (s)
Phase A	A-I	0–48	1000	20	160
	A-II	49–69	1000	35	90
	A-III	70–90	1000	65	50
Phase B	B-I	91–97	500	20	90
	B-II	98–104	500	35	50
	B-III	105–125	500	65	25
Phase C	C-II	126–132	250	35	25
	C-III	133–163	250	65	14

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407 **Table 2** Quality of trickling water during the whole experiment

	BTF1		BTF2	
	Average	Std Dev	Average	Std Dev
pH	8.91	0.23	9.01	0.23
Conductivity (mS cm^{-1})	5.22	1.33	5.23	1.14
Nitrate conc.(mg N L^{-1})	30	23	38	33
Soluble COD (mg L^{-1})	1200	498	1107	540

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Figure Captions

Fig. 1 Schematic of the experimental set-up for the determination of k_La

Fig. 2 Schematic of the experimental set-up for the elimination of isopropanol

Fig. 3 Influence of superficial liquid velocity on the oxygen mass transfer coefficient in BTFs

Fig. 4 Influence of superficial gas velocity on the oxygen mass transfer coefficient for the structured packing material

Fig. 5 Outlet pattern emission during 24 hours monitoring of the biotrickling filtration of isopropanol under intermittent loading conditions for BTF2 a) Phase A-III b) Phase B-II

Fig. 6 Performance of the BTFs on the removal of isopropanol. Discontinuous line represents a 1.8 step increase in the inlet load a) BTF1 b) BTF2

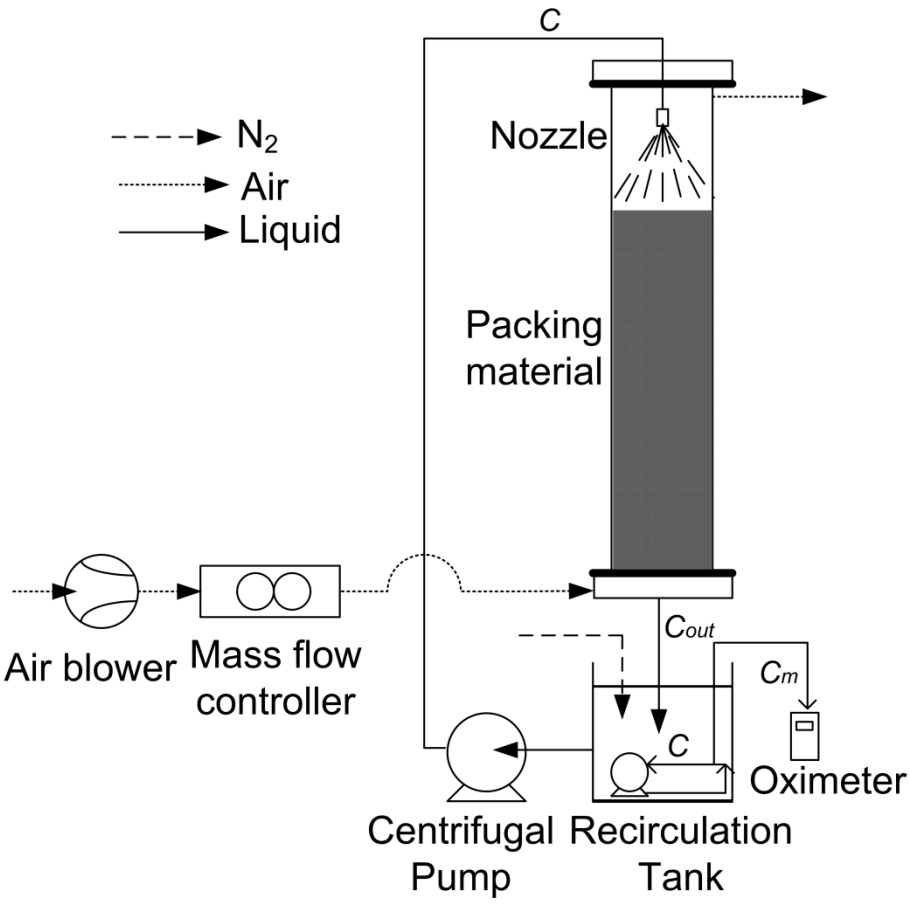
Fig. 7 Isopropanol elimination capacity versus inlet load a) BTF1 b) BTF2

Fig. 8 Production of carbon dioxide versus elimination capacity of isopropanol a) BTF1 b) BTF2

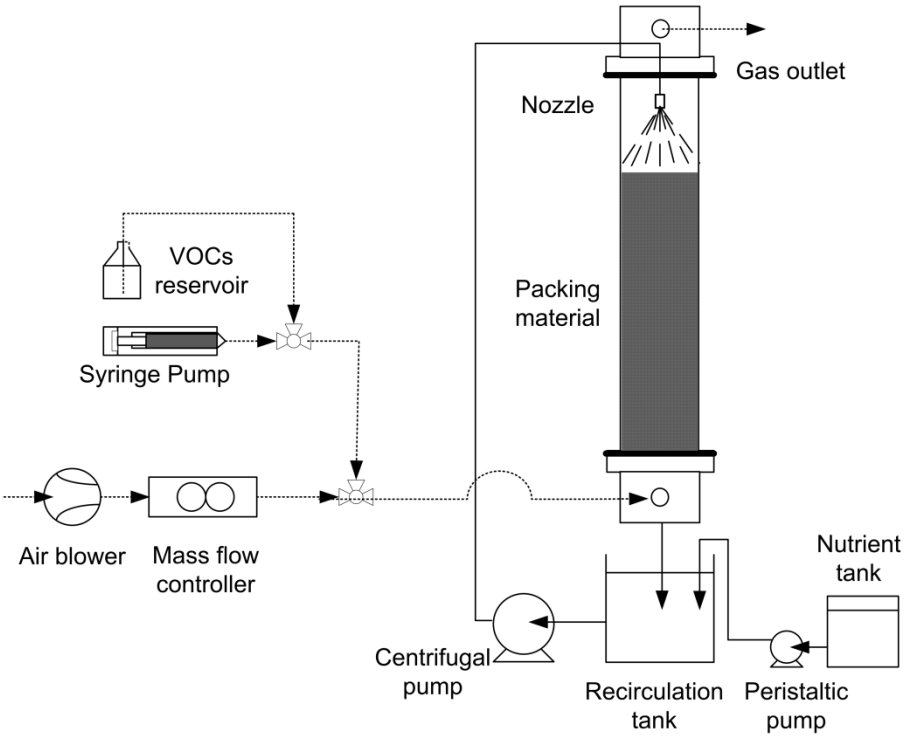
Fig. 9 Influence of the spraying regime on the outlet pattern emission a) spraying 15 minutes every 1.5 hours during VOC feeding period b) spraying 15 minutes every 3 hours during VOC feeding period c) 15 minutes every 3 hours during 24 hours

Fig. 10 Performance of the BTFs on the removal of isopropanol after 7 weeks of starvation a) BTF1 b) BTF2

Fig. 1 Schematic of the experimental set-up for the determination of k_La



435 **Fig. 2** Schematic of the experimental set-up for the elimination of isopropanol



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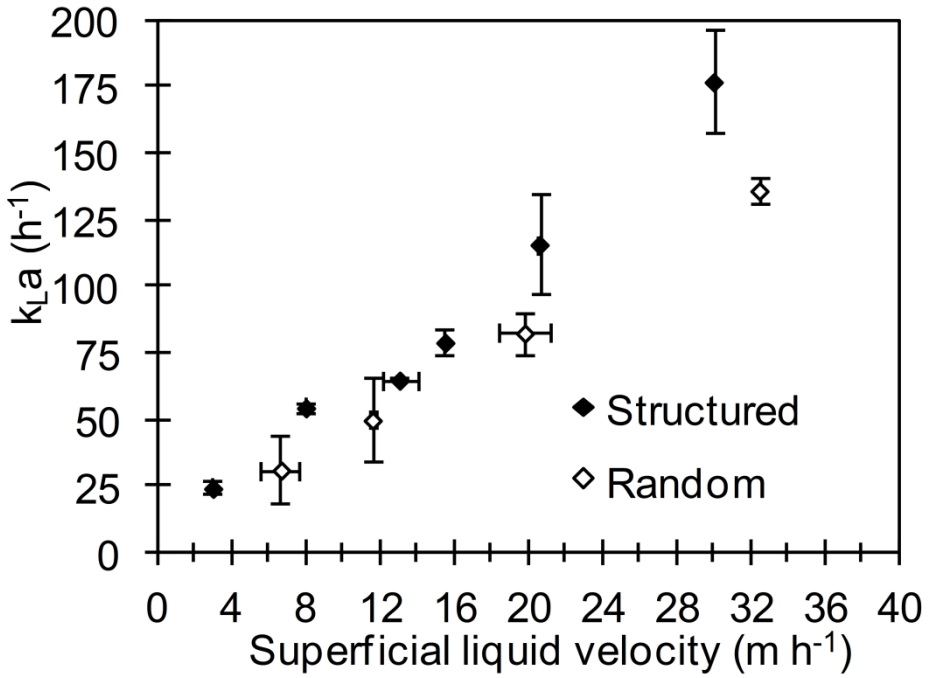
438 **Fig. 3** Influence of superficial liquid velocity on the oxygen mass transfer coefficient in BTFs



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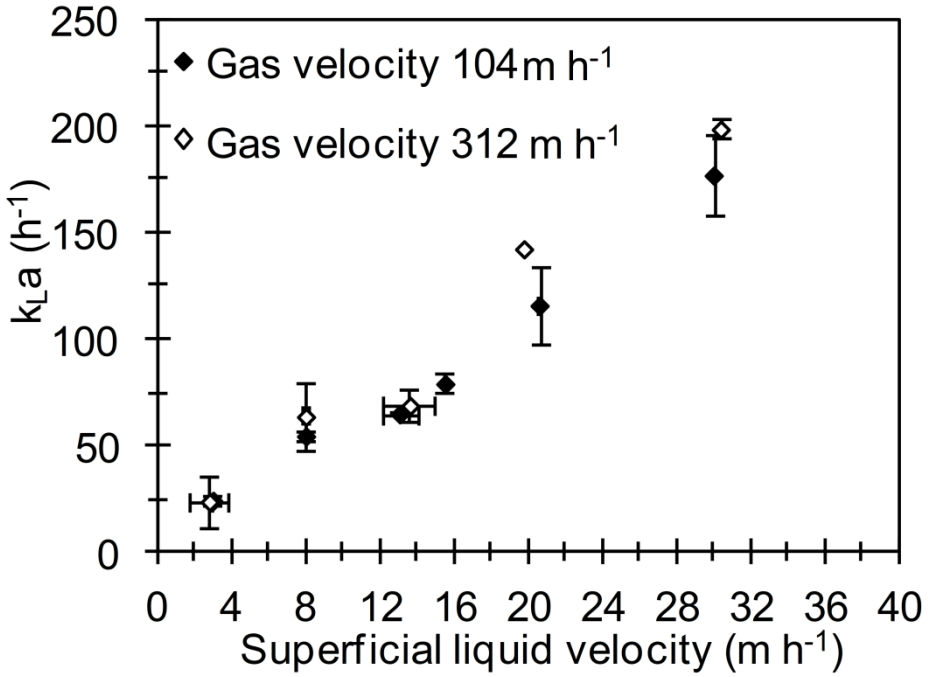
441 **Fig. 4** Influence of superficial gas velocity on the oxygen mass transfer coefficient for the structured

442 packing material



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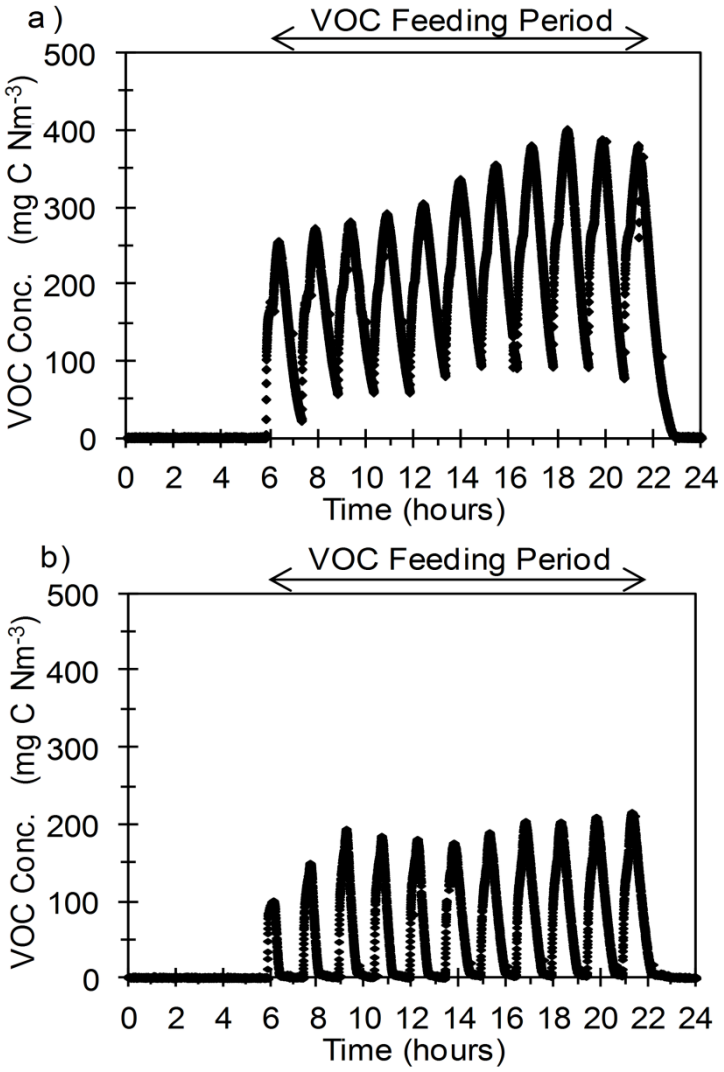
445 **Fig. 5** Outlet pattern emission during 24 hours monitoring of the biotrickling filtration of isopropanol

446 under intermittent loading conditions for BTF2 a) Phase A-III b) Phase B-II



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449 **Fig. 6** Performance of the BTFs on the removal of isopropanol. Discontinuous line represents a 1.8 step

450 increase in the inlet load a) BTF1 b) BTF2

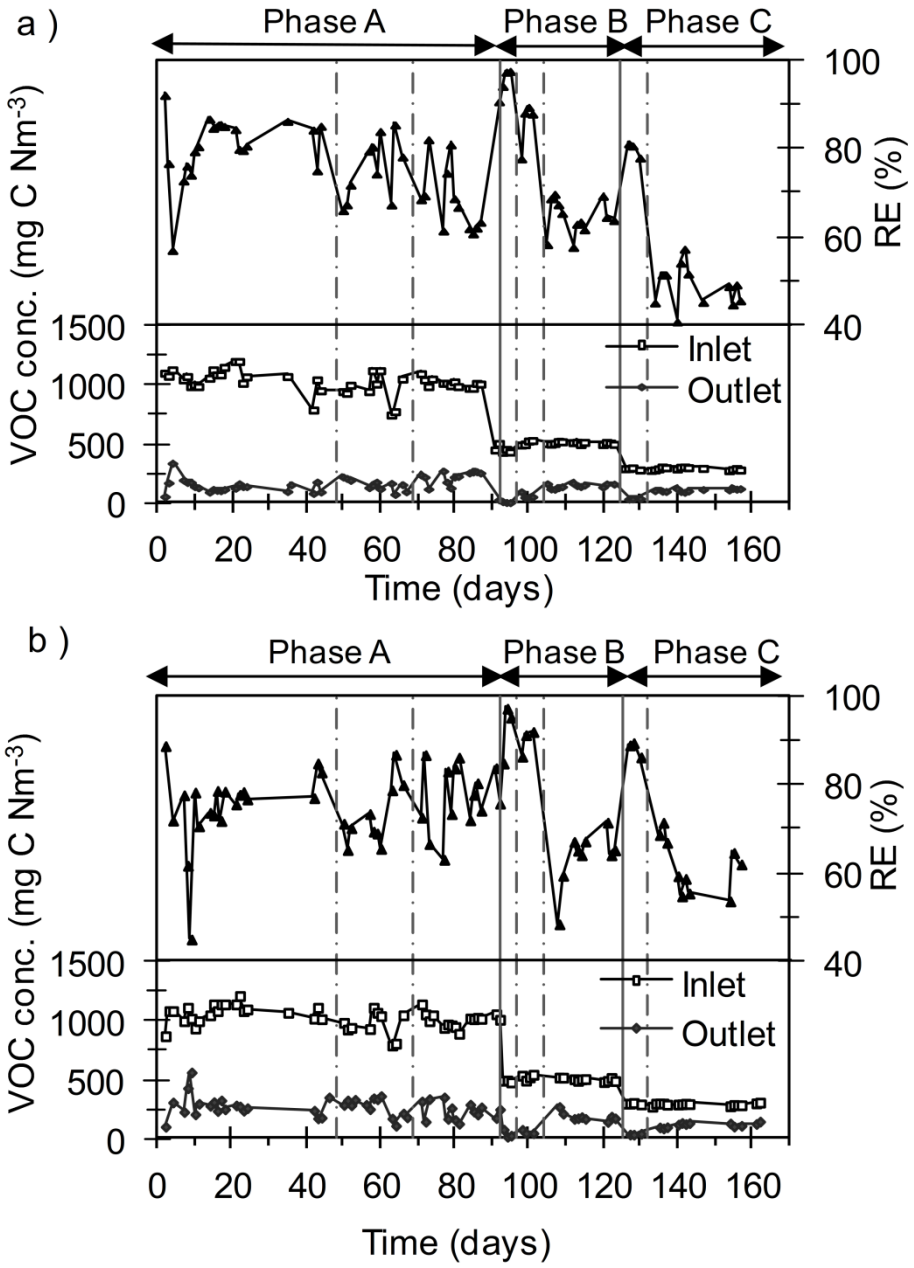

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Fig. 7 Isopropanol elimination capacity versus inlet load a) BTF1 b) BTF2

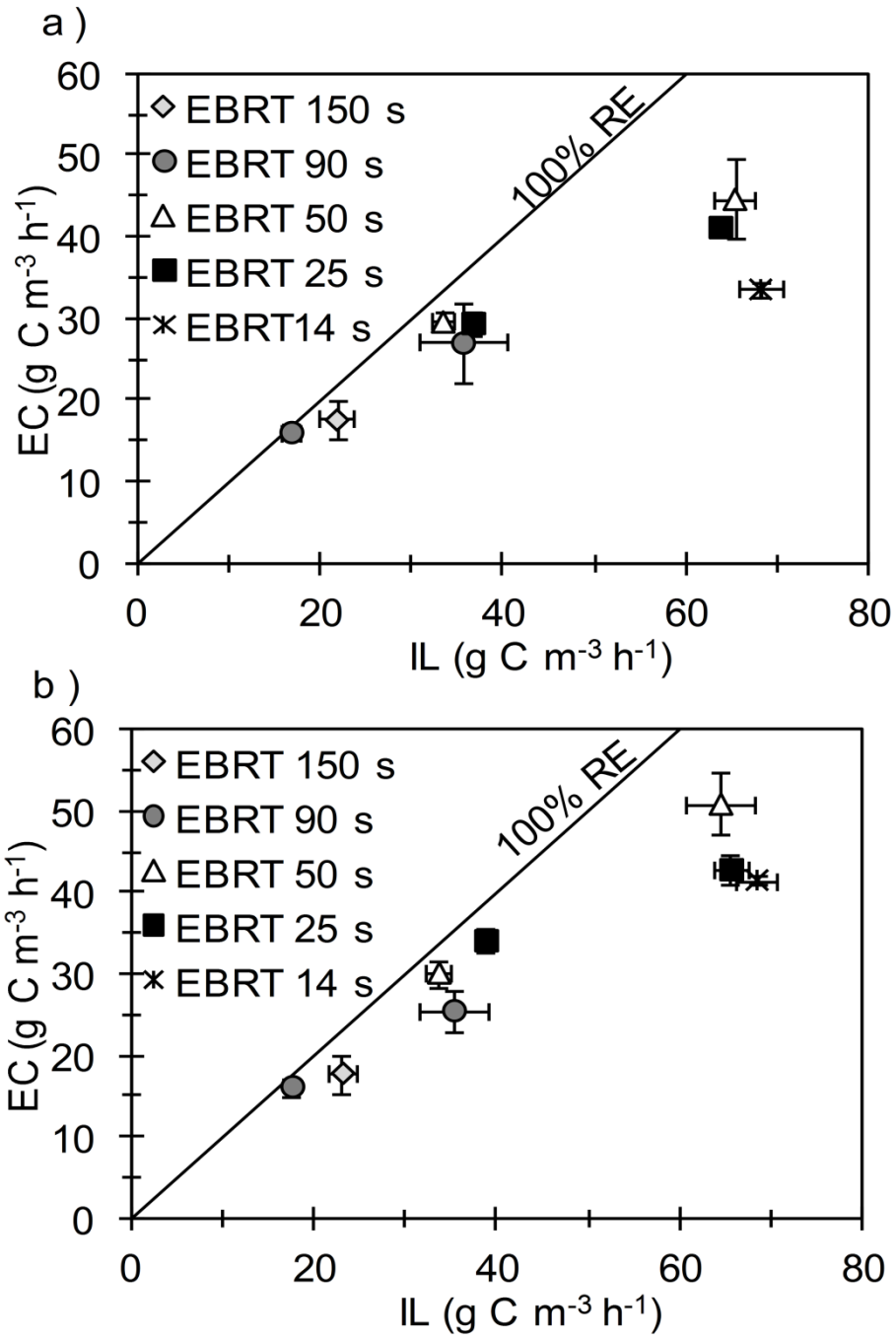
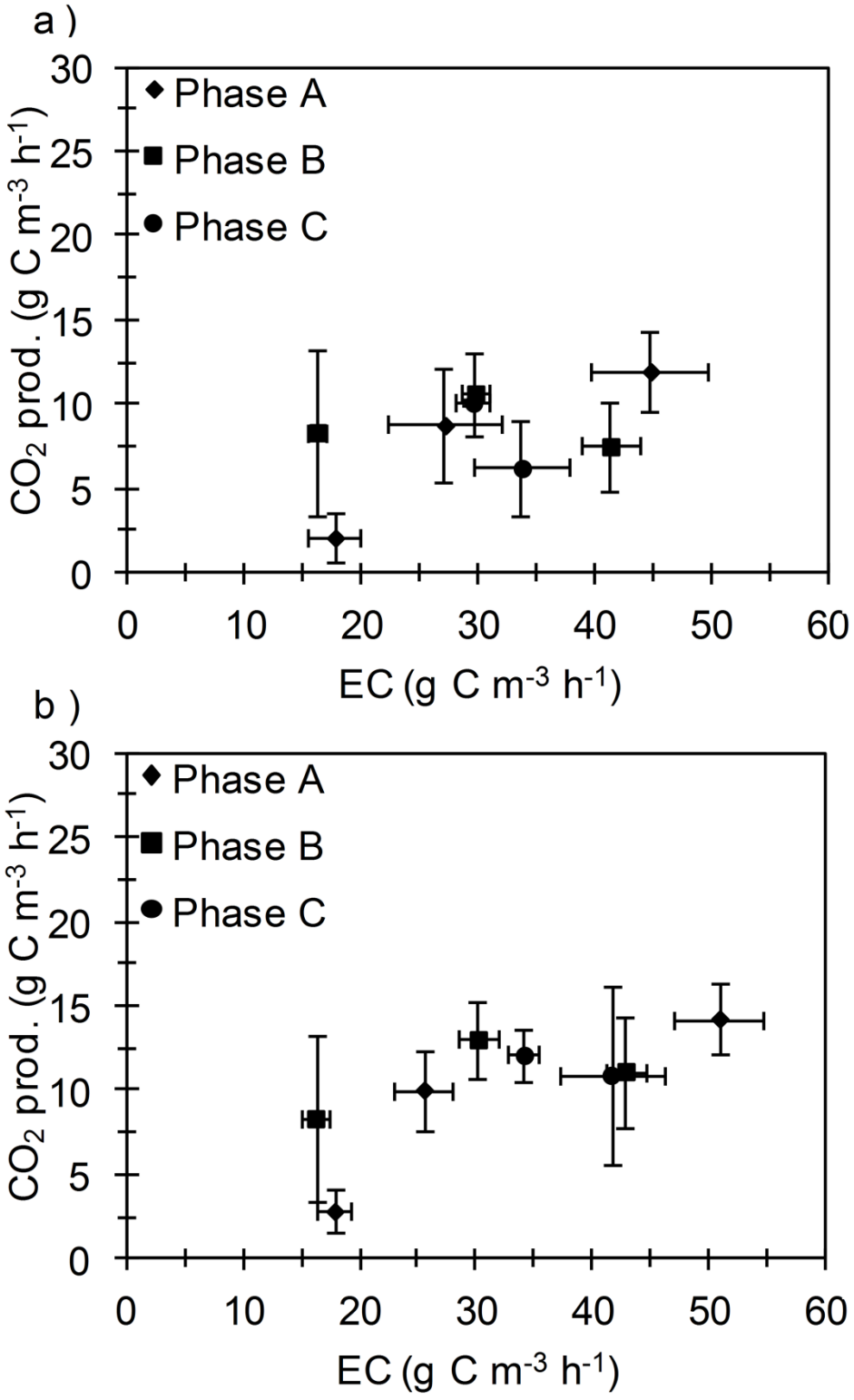


Fig. 8 Production of carbon dioxide versus elimination capacity of isopropanol a) BTF1 b) BTF2



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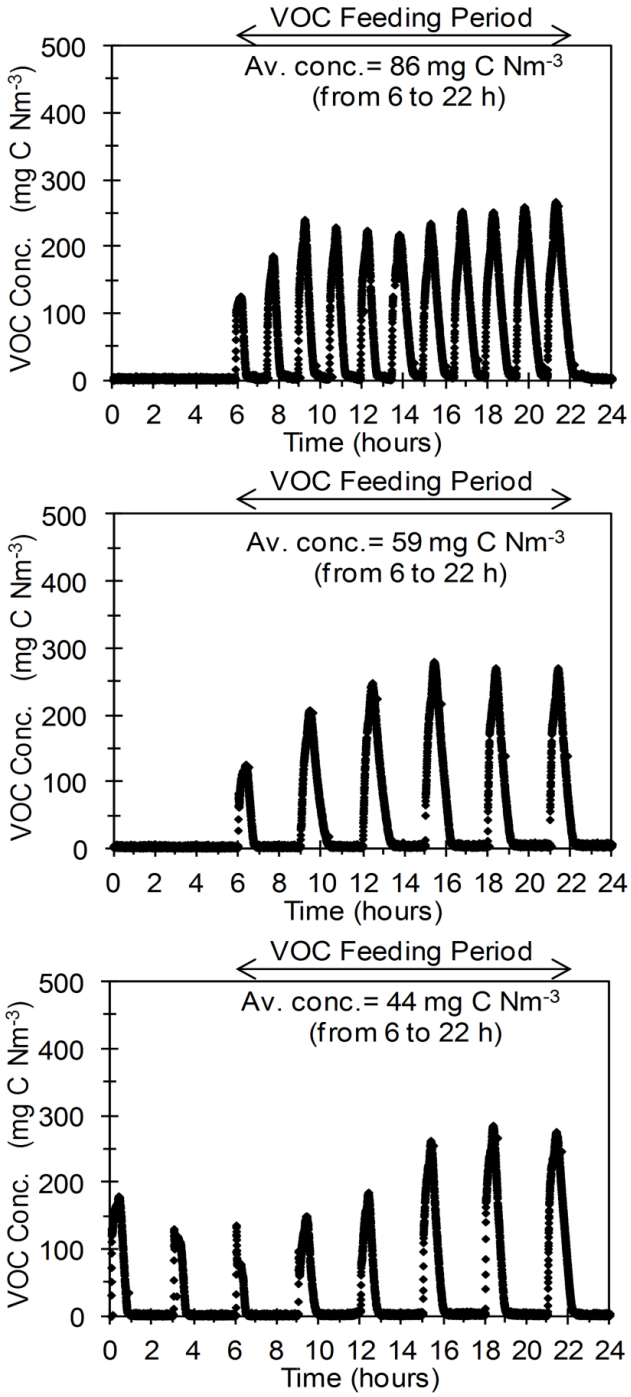
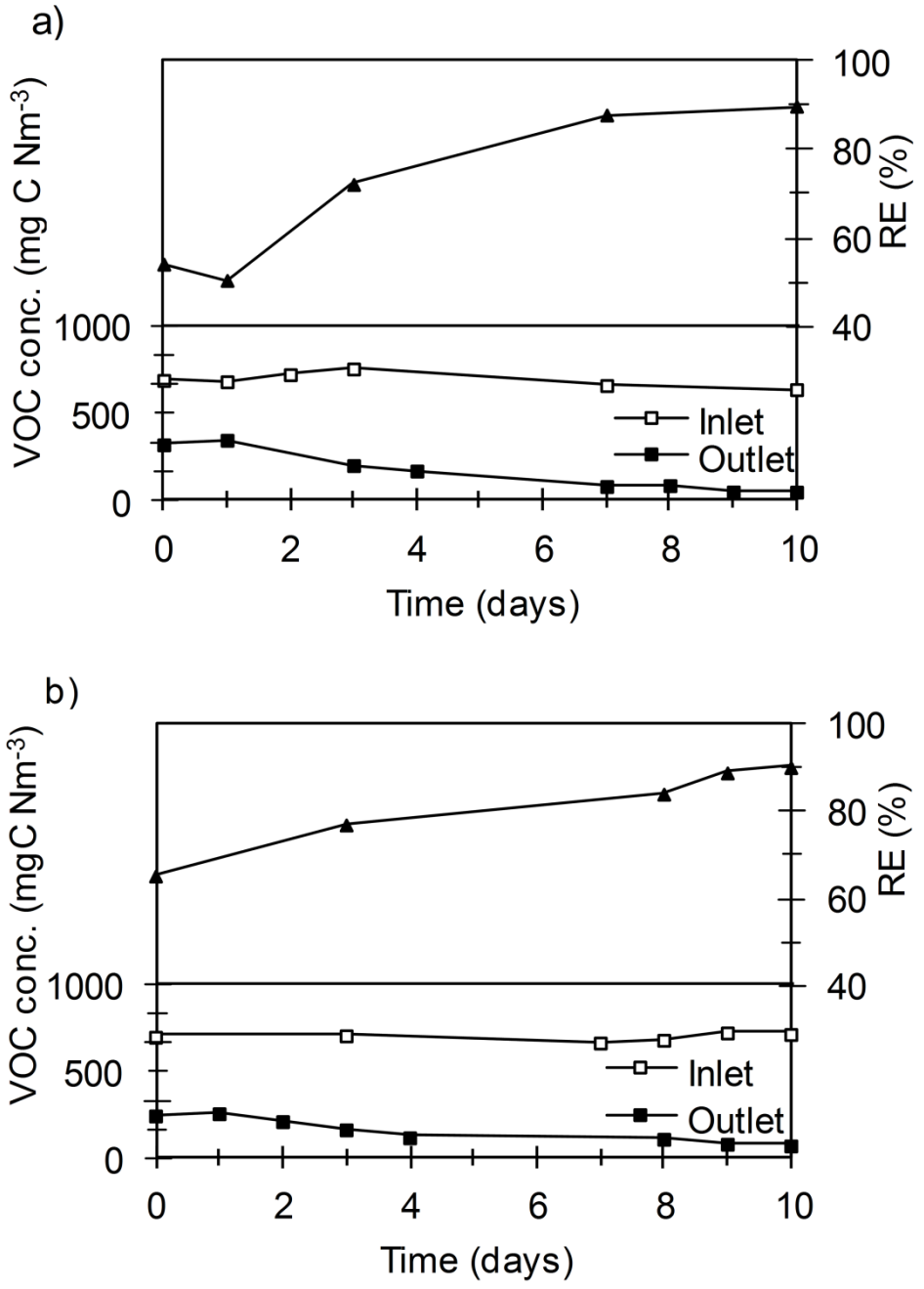


464 **Fig. 10** Performance of the BTFs on the removal of isopropanol after 7 weeks of starvation a) BTF1 b)

465 BTF2



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