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Research article

Release of formaldehyde during the biofiltration of methanol vapors in a peat biofilter inoculated with *Pichia pastoris* GS115

Karlo Guerrero, Alejandra Arancibia, Manuel Caceres, German Aroca *

Escuela de Ingeniería Bioquímica, Facultad de Ingeniería, Pontificia Universidad Católica de Valparaíso, Av. Brasil 2085, Valparaíso, Chile

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ABSTRACT

Background: Methanol can be effectively removed from air by biofiltration. However, formaldehyde is one of the first metabolic intermediates in the consumption of methanol in methylotrophic microorganisms, and it can be released out of the cell constituting a secondary emission.
Results: The total removal of methanol was achieved up to input loads of 263 g m^{-3} h^{-1} and the maximum elimination capacity of the system was obtained at an empty bed residence times of 90 s and reached 330 g m^{-3} h^{-1} at an input methanol load of 414 g m^{-3} h^{-1} and 80% of removal efficiency. Formaldehyde was detected inside the biofilter when the input methanol load was above 212 g m^{-3} h^{-1}. Biomass in the filter bed was able to degrade the formaldehyde generated, but with the increase of the methanol input load, the unconsumed formaldehyde was released outside the biofilter. The maximum concentration registered at the output of the system was 3.98 g m^{-3} when the methanol load was 672 g m^{-3} h^{-1} in an empty bed residence times of 60 s.
Conclusions: Formaldehyde is produced inside a biofilter when methanol is treated in a biofiltration system inoculated with *Pichia pastoris*. Biomass present in the reactor is capable of degrading the formaldehyde generated as the concentration of methanol decreases. However, high methanol loads can lead to the generation and release of formaldehyde into the environment.
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1. Introduction

Methanol (CH_3OH) is one of the most important building blocks in chemical industry [1], it is used as solvent, co-solvent and feedstock to synthesize chemicals derivatives such as methyl and vinyl acetates, methylamines, methyl-ter-buthyl-ether (MTBE) and acetic acid [2,3]. It can be synthesized from several carbon-containing feedstocks including natural gas, coal and biomass [4]. Global losses of methanol vapors to the atmosphere during manufacture, use and disposal have not been completely evaluated but are likely to be substantial [5]. In 2017, only in United States, 55,376 tons of methanol were emitted to the atmosphere [6]. It shows the importance of developing efficient and reliable technologies for the removal of this contaminant from industrial waste gases.

Several authors have shown that methanol can be effectively removed from air by biofiltration [5,7,8,9,10,11,12,13,14,15,16] and a wide variety of methylotrophic microorganisms have been found in biofilters treating methanol emissions: *Pseudomonas* sp., *Methylobacterium* sp., *Methylococcus* sp., *Scytalidinum* sp. [13] and some yeast such as *Pichia*, *Torulopsis*, *Kloeckera*, *Rhodotorula*, and *Candida* [8]. The methylotrophic yeast *Pichia pastoris* has been used in methanol biofiltration in order to simultaneously obtain a valuable product: heterologous proteins [8,14,15]. *P. pastoris* is an eukaryotic organism that reaches high cell densities in economical culture media and has an efficient methanol inducible promoter [17]. It has a metabolic pathway that involves as a first reaction the conversion of methanol to formaldehyde by FAD-linked alcohol-oxidase (AOX) [18]. Because of its low molecular weight formaldehyde can diffuse the cellular membrane and it could be found in the outlet of a biofilter treating air contaminated with methanol vapors. However, the generation of formaldehyde during methanol biofiltration has not been reported until now, although the presence of toxic intermediaries in other biofiltration processes has been described.

Devinny and Hodge [19] observed the accumulation of metabolic intermediaries during the biofiltration of ethanol, in their research they conclude that the application of high ethanol feed rates would be associated with the release of acetaldehyde, acetic acid and ethyl acetate. On the other hand Deshusses et al. [20], investigating the biofiltration of high charges of ethyl acetate in the presence of toluene,

* Corresponding author.
E-mail address: german.aroca@pucv.cl (G. Aroca).
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reported the formation of ethanol, a metabolic intermediate of the degradation pathway of this compound. Ethanol concentrations of up to 5% of the entry value of the ethyl acetate concentration were registered; an interesting conclusion of this work is the relation between the formation of metabolism intermediaries and the biofiltration of high loads of polar volatile organic compounds (VOC). In a similar way, the research carried out by Christen et al. [21], studied the removal of ethanol vapors, using in this case a pure culture of the yeast *Candida utilis*, through the use of global carbon balances they were able to establish that only 64% of the available carbon is used in the production of CO_2, while 7.8% and 20.4% are released as acetaldehyde and ethyl acetate, respectively.

The formaldehyde generation and its potential release during the methanol biofiltration process are especially worrisome, due to the high toxicity for humans [22]. In fact, even at concentrations between 0.03 and 1.7 ppm it can produce reactions such as: ocular irritation, profuse lacrimation, nasal obstruction, irritation of the throat and cough [23]; over 10 ppm it causes a sensation of suffocation and damage to the central nervous system [24]. Moreover, formaldehyde has been classified as a human carcinogen by the International Agency for Research of Cancer (IARC) [25]. As a potent electrophile, its toxicity stems from its ability to react rapidly with nucleophilic components of DNA, RNA and proteins, leading to protein and DNA damage in the form of crosslinking [26].

The aim of this work was to evaluate the performance of a laboratory scale biofilter, packed with a mixed bed of peat and granular perlite inoculated with *P. pastoris*, a methylotrophic yeast, to assess the appearance of formaldehyde along the biofilter and its fate depending on the loading rate of methanol.

2. Materials and methods

2.1. Microorganism maintenance and inoculum preparation

P. pastoris GS115 was used to inoculate the biofilters. It was grown in YPD medium, with a composition of 10 g L^{-1} yeast extract, 20 g L^{-1} peptone and 20 g L^{-1} dextrose. Dextrose solution was autoclaved separately to avoid caramelization. The propagation was carried out in 250 mL in Erlenmeyer flask incubated at 30°C and agitated at 250 rpm for 36 h. The inoculum for the biofilter was grown in a 5 L bioreactor (New Brunswick, New Jersey, USA) using 2.5 g L^{-1} methanol as carbon and energy source, the composition of the culture medium was 4 g L^{-1} KH_2PO_4, 4 g L^{-1} $(NH_4)_2SO_4$, 0.38 g L^{-1} $CaCl_2$, 18.2 g L^{-1} K_2SO_4, 9.4 g L^{-1} $MgSO_4 \cdot 7H_2O$, 1 g L^{-1}, and supplemented with 1.0 g L^{-1} of yeast extract. The operation conditions were: 3 L working volume, temperature controlled at 30°C, agitation at 550 rpm, 3 L min^{-1} of aeration, and pH controlled at 5.5 by the addition of a 1 N solution of NaOH. The reactor was previously sterilized in autoclave at 121°C and 1 atm.

2.2. Filter bed preparation

The material used as support in the biofilter was prepared mixing 60% peat and 40% perlite (v/v) [5]. Peat has high amounts of organic matter, high specific surface area, good water holding capacity and good permeability [27]. In this medium, peat was used to support the biofilm and supply microbial nutrients [28] and perlite to keep humidity and decrease the pressure drop across the filter medium. Crushed oyster shell, a source of calcium carbonate, was added as a pH buffer at 130 g kg^{-1} of dry filter media [29].

For preparing the inoculum of the biofilter, *P. pastoris* GS115 was harvested from its culture media by centrifugation and suspended in a fresh sterile mineral solution with the following composition: 0.450 g L^{-1} KH_2PO_4, 0.015 g L^{-1} NaCl, 0.070 g L^{-1} $MgSO_4 \cdot 7H_2O$ and 0.003 g L^{-1} $FeCl_3 \cdot 6H_2O$, the cell suspension was adjusted until a concentration of 2.5 g L^{-1} and added to the filter material in 20% (v/v) and mixed in until complete absorption of the solution in a mechanical mixer. The physicochemical properties of the resulting support material are shown in Table 1.

2.3. Biofiltration system

A laboratory-scale biofilter was set up using 90 cm of a transparent acrylic tube with an internal diameter of 9.8 cm, the total packing volume was 5.5 L. The biofilter had twenty equidistant gas sampling ports (every 5 cm) along the height of the column. The gas fed into the biofilters was prepared by mixing two air streams, one passed through a contact column containing methanol at 99.5% purity (Panreac, Barcelona, Spain), while the second passed through out another column containing distilled water, as humidification system. These streams were mixed to generate the feed flow with the required concentration of methanol. Gas flow was controlled using correlated flowmeters (Gilmont Cole Palmer, Illinois, USA), pressure regulator and high precision needle valves (Cole Palmer, Ilinois, USA), all connections were made using Kynar 1/4 OD tubing (Cole Palmer, Illinois, USA). A diagram of this system is shown in Fig. 1. The reactor was operated with an upward flow and during all the experiment the biofilter were kept at room temperature 20–25°C.

2.4. Startup and operation of the biofiltration system

For starting up the biofiltration system, a typical starting strategy was used which consists in the use of low pollutant inlet concentrations together with low gas flow velocities and a gradual increase of the input load to the system [30]. For this purpose, an initial methanol inlet concentration of 1.5 g m^{-3} was fed at a gas flow rate of 0.12 m^3 h^{-1}, corresponding to an empty bed residence time (EBRT) of 160 s, this initial concentration was gradually increased for 15 d, until reaching a concentration of 5 g m^{-3}. In this way, the input load is slightly increased to ensure a quick start-up together with the colonization and acclimatization of the population to high concentrations.

To evaluate the effects of the methanol inlet load on the stability of the system and the release of formaldehyde out of the biofilter, the experiment was done in four stages (Table 2). First, the feed flow rate was fixed at 0.17 m^3 h^{-1}, corresponding to an EBRT of 120 s, and the biofilter was followed for 30 d under three inlet methanol concentrations: 2.5, 5.4 and 8.9 g m^{-3}. Then, from days 46 to 75, the feed flow rate was fixed at 0.22 m^3 h^{-1}, corresponding to an EBRT of 90 s, and the inlet methanol concentration was varied from 4.9 to 12.3 g m^{-3}. From days 76 to 105 the feed flow rate was fixed at 0.33 m^3 h^{-1}, corresponding to an EBRT of 60 s, and the inlet methanol concentration was varied from 3.9 to 11.2 g m^{-3}. Finally, for the latest 15 d, tests were carried out to determine the stability of the system regarding the increase of methanol inlet load up to values above the limit of the elimination capacity of the system. During that period, the concentrations of methanol were increased until 16.5 g m^{-3} at an EBRT of 60 s, in order to exceed the degradation capacity of the biofilter. Stepwise changes in concentration at each EBRT were used to replicate a wide range of conditions that could be expected in an industrial setting. The methanol inlet concentration and EBRT were adjusted by changing the airflow through the methanol reservoir as well as the total air entering the system.

Table 1
Physicochemical properties of the biofilter media.

Moisture content (%)	63 ± 0.21
Density (g mL^{-1})	0.42 ± 0.07
Void fraction (%)	66.83 ± 0.42
pH	5.5 ± 0.06
Ash (% dry weight)	4.5 ± 0.27
Organic matter (% dry weight)	93.7 ± 0.74
Total nitrogen (% dry weight)	2.1 ± 0.15

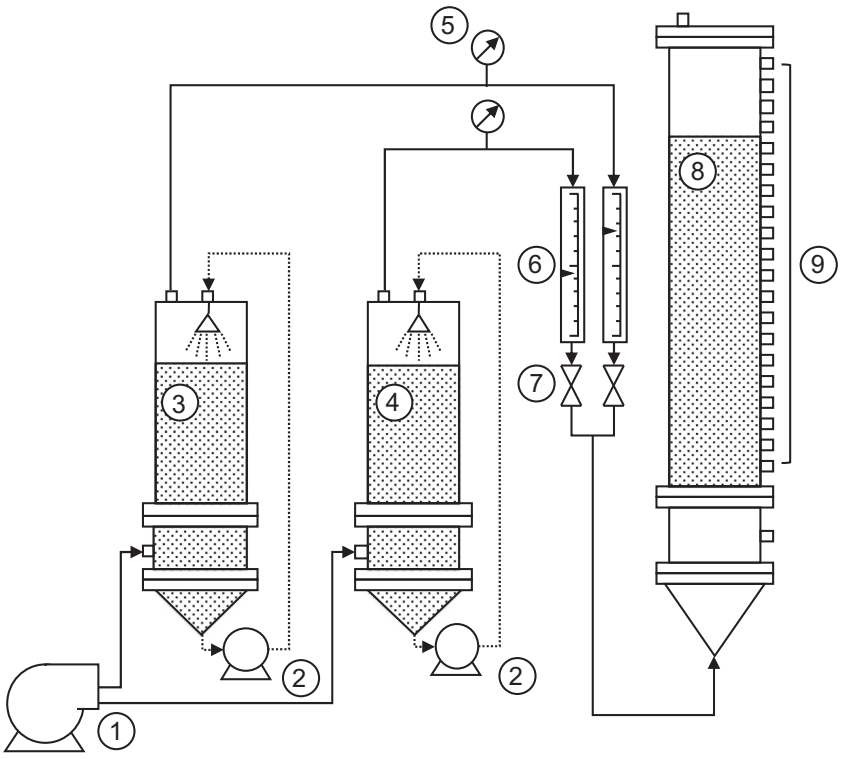

Fig. 1. Diagram of the laboratory-scale experimental biofiltration system. (1) Air supply. (2) Recirculation pumps. (3) Methanol saturation system. (4) Humidification system. (5) Manometers. (6) Flowmeters. (7) Needle valves. (8) Biofilter. (9) Sampling ports.

The variables and parameters used to characterize the operation of the biofilters were Inlet Load (IL; g m^{-3} h^{-1}); Elimination Capacity (EC; g m^{-3} h^{-1}); and Removal Efficiency (RE, %), according to Equation 1, Equation 2, Equation 3 and Equation 4 [31].

$$EBRT = \frac{V_r}{Q} \quad \text{[Equation 1]}$$

$$EC = \frac{Q}{V_r}(C_{in} - C_{out}) \quad \text{[Equation 2]}$$

$$IL = \frac{Q}{V_r} \cdot C_{in} \quad \text{[Equation 3]}$$

$$\%RE = \left[\frac{(C_{in} - C_{out})}{C_{in}} \cdot 100\right] \quad \text{[Equation 4]}$$

where Q and V_r are the polluted air flow (m^3 h^{-1}) and bioreactor volume (m^3) respectively, while C_{in} and C_{out} are the inlet and outlet methanol concentrations (g m^{-3}).

2.5. Analytical methods

Methanol and formaldehyde concentrations were measured using a gas chromatograph (Clarus 500, Perkin Elmer, USA) equipped with an Hayesep Q column (Agilent, USA) and a flame ionization detector (FID). Oven temperature was 130°C, while both the injector and detector temperature were 150°C. Under these conditions, the retention time for methanol and formaldehyde were 2.5 and 3.5 min respectively.

3. Results and discussion

3.1. Performance of the biofiltration system during the operation

A fast start-up was obtained when using concentrated inoculum of the methylotrophic yeast *P. pastoris*. Fig. 2 shows that in 15 d, the methanol elimination capacity increased until 108.9 g m^{-3} h^{-1}, while the removal efficiency reached values above 93% at an EBRT of 160 s.

When the EBRT was decreased to 120 s the elimination capacity increases from 86.4 g m^{-3} h^{-1} to 270.9 g m^{-3} h^{-1} in 30 d of operation with removal efficiency between 98 to 100%. Operating at an EBRT of 90 s, the system reached a maximum elimination

Table 2
Operational conditions for evaluating biofilter performance during different stages of the experiment.

		Operation time				
		Start up: from day 0 to 15	Stage 1: from day 16 to 45	Stage 2: from day 46 to 75	Stage 3: from day 76 to 105	Stage 4 (Overload): from day 106 to 119
Gas flow rate	m^3 h^{-1}	0.12	0.17	0.22	0.33	0.33
EBRT	s	160 s	120 s	90 s	60 s	60 s
Methanol inlet concentration	g m^{-3}	From 1.5 to 5	2.70 5.40 8.90	4.90 9.80 12.3	3.90 8.20 11.2	From 11 to 16.5

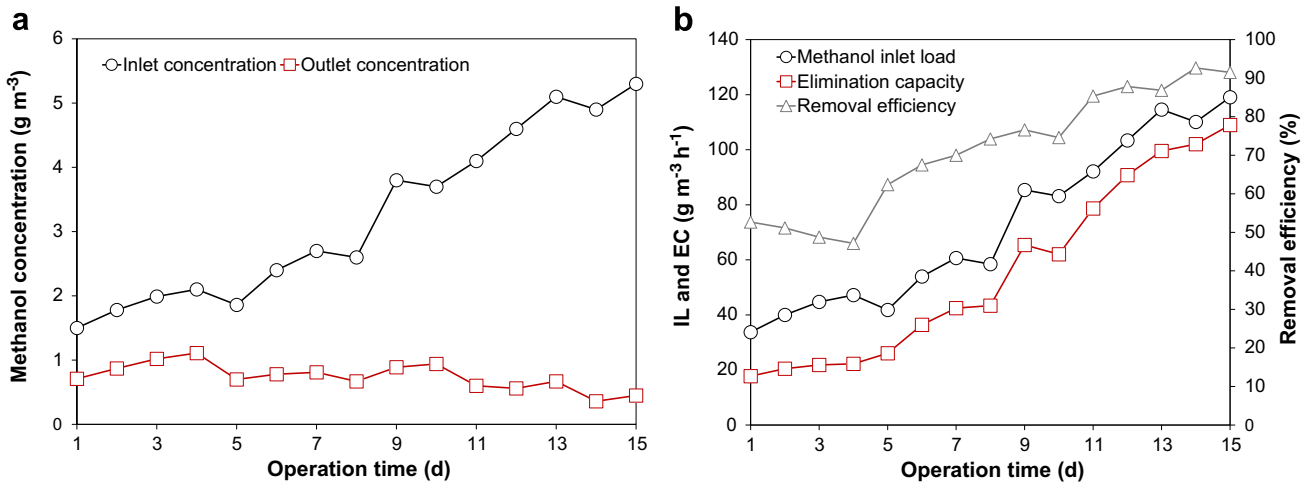

Fig. 2. (a) Methanol inlet and outlet concentrations during the startup of the biofiltration system. (b) Methanol inlet load, elimination capacity and removal efficiency during the startup of the biofiltration system.

capacity of 330 g m^{-3} h^{-1} with 80% of removal efficiency on day 66 (Fig. 3a and Fig. 3b), while at an EBRT of 60 s the maximum elimination capacity was 338 g m^{-3} h^{-1} with 69% of removal efficiency on day 93.

At an EBRT of 120 s, there was 100% of removal under a wide range of methanol inlet concentrations, from 2.7 up to 9.3 g m^{-3}, while at lower EBRT the concentrations at which high removal efficiency were reached decrease as results of the increase of the inlet load. In this way at 90 s

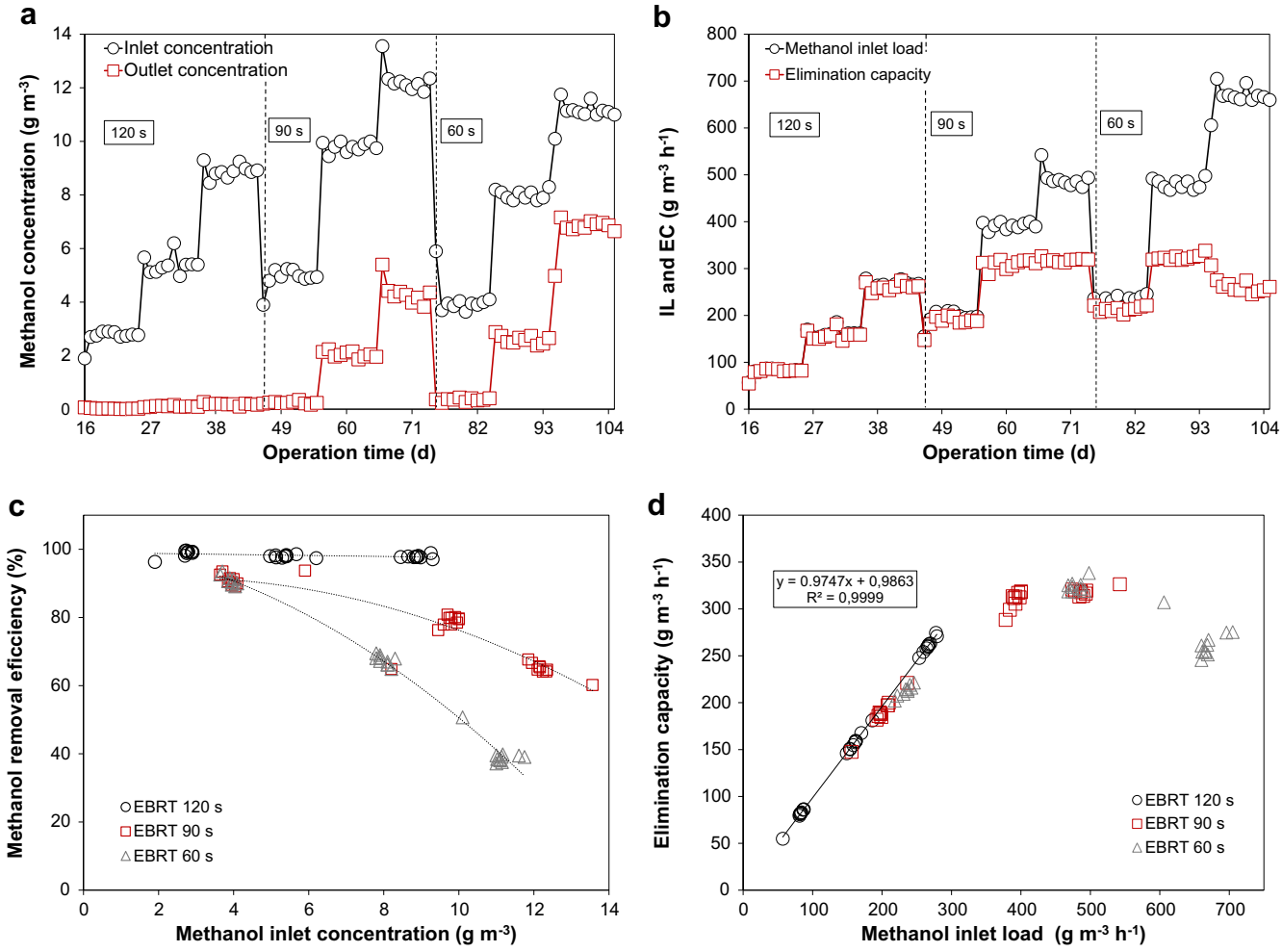

Fig. 3. (a) Variation of the inlet and outlet methanol concentration during the 90 d of operation. (b) Variation of the inlet methanol load and elimination capacity during the 90 d of operation. (c) Variation of the removal efficiency versus the inlet concentration at three EBRT. (d) Elimination capacity versus the methanol inlet load at three EBRT, the straight line represents 100% of removal.

EBRT there was a maximum of 95% of removal efficiency with a methanol inlet concentration of 5.1 g m^{-3} on day 51, while at 60 s EBRT a maximum removal efficiency of 93% was reached with a methanol inlet concentration of 3.9 g m^{-3} on day 82 (Fig. 3c).

The overall performance of the system is described in terms of the elimination capacity versus methanol inlet load, in this relation a straight line represent 100% of removal efficiency [32]. From Fig. 3d the critical inlet load is 263 g m^{-3} h^{-1}, above this value the removal efficiency decreases. In biofilters treating methanol, the critical inlet load has been reported in the range of 100 to 280 g m^{-3} h^{-1} [7,11], they are in agreement with the results reported here. For biotrickling filters, critical inlet load up to 500 g m^{-3} h^{-1} has been reported [33]. The continuous trickling of the aqueous nutrient solution in a biotrickling filter is probably the reason for the better performance when water-soluble VOCs are treated [27,34], together with the small partition coefficient of methanol in an air–water system [35].

The maximum elimination capacity achieved in this work was slightly higher than that reported in previous works: Shareefdeen et al. [5] reached removal capacities up to 112.8 g m^{-3} h^{-1} with 100% of removal efficiency, Krailas et al. [7] reported a maximum elimination capacity of approximately 101 g m^{-3} h^{-1} with an optimum methanol inlet load of 169 g m^{-3} h^{-1}, and Prado et al. [11] worked with loads between 120 and 280 g m^{-3} h^{-1} obtaining removal efficiency between 95 and 99%.

Table 3 summarizes the results obtained during the first three stages of the experiment, the average values for each steady state are shown with their standard deviation.

3.2. Generation of formaldehyde during the operation of the biofiltration system

The generation of formaldehyde along the biofilter was determined at each stage of the experiment. Fig. 4a, Fig. 4b and Fig. 4c show the variation of the formaldehyde and methanol concentration in the height of the biofilter at EBRT of 120, 90 and 60 s at three methanol inlet concentrations for each EBRT. The curves show the average values and standard deviation obtained during the operation at each combination of methanol input concentration and EBRT at steady state.

Formaldehyde was detected inside the biofilter in almost all the stages of the experiment. Only at 120 s EBRT and methanol inlet concentration of 2.7 g m^{-3} no formaldehyde was detected inside, while at the same EBRT and methanol inlet concentrations of 5.4 and 8.9 g m^{-3} the maximum formaldehyde concentrations measured within the biofilter were 0.45 and 1.32 g m^{-3} respectively. At 90 s EBRT formaldehyde was detected in all methanol inlet concentrations, at this stage of the experiment the maximum formaldehyde concentration inside the biofilter was 2.45 g m^{-3} at an inlet methanol concentration of 12.3 g m^{-3} that corresponds to a methanol inlet load of 491 g m^{-3} h^{-1}. Similarly, at 60 s EBRT formaldehyde was detected in all methanol inlet concentrations, being 4.17 g m^{-3} the maximum formaldehyde concentration detected inside the biofilter under an inlet methanol concentration of 11.2 g m^{-3} that corresponds to a methanol inlet load of 672 g m^{-3} h^{-1}.

In all cases, the concentration of formaldehyde keeps stable or decreases when it almost reached 40 cm in height of the biofilter or until the concentration of methanol falls below 2.5 g m^{-3}, it is due to the capacity of methylotrophic microorganisms to consume formaldehyde, favoring the consumption of methanol over any other carbon source [36]. In this case, the decrease in the concentration of methanol produced by the microbial removal inside the biofilter, decreases the availability of the main source of carbon and energy for those microorganisms that are near to the outlet of the reactor, therefore the microorganisms at the top of the biofilter consume the formaldehyde released in the lower part.

In all EBRT used, the generation of formaldehyde increases with the increase's methanol inlet load. At an EBRT of 120 s and methanol inlet concentrations between 2.7 and 5.4 g m^{-3}, formaldehyde was undetectable in the outlet of the biofilter. In this case formaldehyde generated inside the biofilter is completely consumed inside the reactor. When the methanol inlet concentration was increased to 8.9 g m^{-3}, formaldehyde was detected at the outlet of the biofilter at concentrations that not exceed 0.32 g m^{-3}. At 90 s EBRT, the generation of formaldehyde increases as a result of the increase in the input load of methanol. At EBRT of 60 s, formaldehyde release is observed for all methanol input loads used. Formaldehyde at the exit of the biofilter was always detected for methanol input loads of above 212 g m^{-3} h^{-1}, at higher loads the excess is released to the exterior of the biofilter, constituting in a secondary emission, being 3.98 g m^{-3} the maximum concentration of formaldehyde released at an input load of methanol of 672 g m^{-3} h^{-1} (Fig. 4d).

3.3. Performance of the biofiltration system under methanol overload

The effect of the increase of the methanol inlet load above the limit of the elimination capacity of the system on the generation of formaldehyde was determined. Fig. 5a show the variation of the methanol inlet load, elimination capacity and removal efficiency and Fig. 5b show the variation of the inlet and outlet methanol concentration and formaldehyde outlet concentrations respectively, in the overload operation at 60 s EBRT. During the entire overload operation formaldehyde was detected at the biofilter outlet, which reached a maximum concentration of 6.7 g m^{-3} on day 14 at a methanol inlet load of more than 1000 g m^{-3} h^{-1}. From day 4 of the overload operation, the elimination capacity drops gradually from 312 g m^{-3} h^{-1} on day 108 to 91 g m^{-3} h^{-1} on day 115, with removal efficiencies from 38 to 9%.

4. Conclusion

Formaldehyde is produced inside a biofilter when an emission of methanol is treated in a biofiltration system inoculated with the

Table 3
Performance of the biofiltration system obtained during the first three stages of the experiment, the average values are presented with their standard deviation for each steady state.

EBRT s	Methanol inlet concentration g m^{-3}	Methanol outlet concentration g m^{-3}	Methanol inlet load g m^{-3} h^{-1}	Elimination capacity g m^{-3} h^{-1}	Removal efficiency %	Formaldehyde outlet concentration g m^{-3}
120 s	2.70 ± 0.29	0.03 ± 0.02	81.12 ± 8.77	80.28 ± 9.22	98.88 ± 1.00	Not detected
	5.40 ± 0.34	0.11 ± 0.02	161.88 ± 10.31	158.61 ± 9.97	97.98 ± 0.37	Not detected
	8.90 ± 0.25	0.19 ± 0.04	266.88 ± 2.00	261.18 ± 7.60	97.86 ± 0.45	0.27 ± 0.05
90 s	4.90 ± 0.38	0.25 ± 0.05	195.96 ± 15.33	186.12 ± 14.77	94.97 ± 0.91	Not detected
	9.80 ± 0.18	2.05 ± 0.11	391.79 ± 7.15	309.79 ± 9.59	79.06 ± 1.36	0.52 ± 0.08
	12.30 ± 2.08	4.34 ± 1.32	491.95 ± 83.11	318.48 ± 30.99	64.81 ± 9.36	2.21 ± 0.60
60 s	3.90 ± 1.37	0.36 ± 0.80	234.20 ± 81.98	212.53 ± 34.47	90.77 ± 8.30	0.62 ± 0.53
	8.20 ± 0.69	2.82 ± 0.77	492.00 ± 41.18	322.74 ± 7.87	66.00 ± 5.49	2.47 ± 0.50
	11.20 ± 0.26	6.87 ± 0.15	672.12 ± 15.54	259.98 ± 9.95	38.67 ± 0.88	3.98 ± 0.57

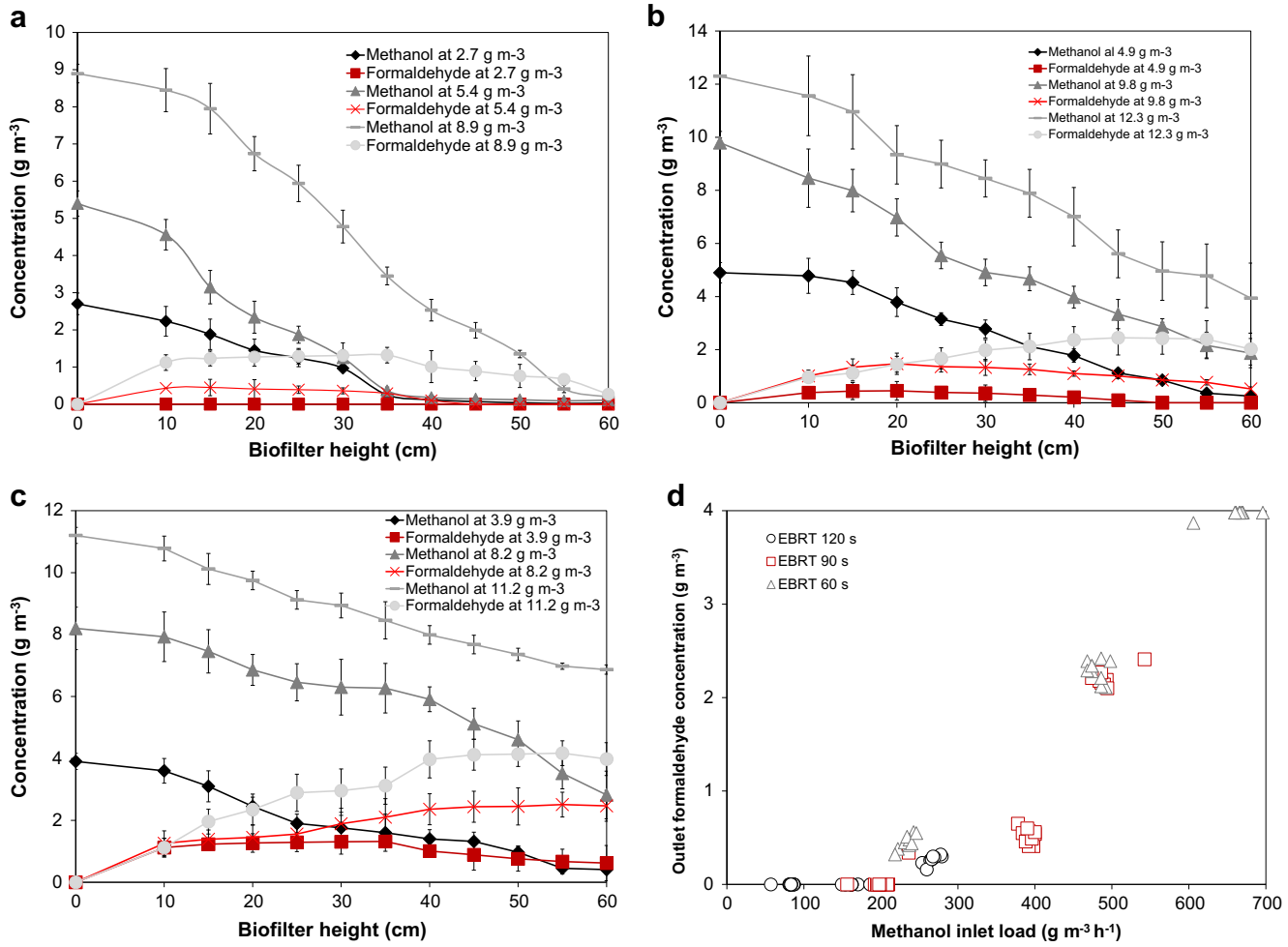

Fig. 4. (a) Variation of the concentration of methanol and formaldehyde in the height of the biofilter at different methanol inlet concentrations in an EBRT of 120 s. (b) Variation of the concentration of methanol and formaldehyde in the height of the biofilter at different methanol inlet concentrations in an EBRT of 90 s. (c) Variation of the concentration of methanol and formaldehyde in the height of the biofilter at different methanol inlet concentrations in an EBRT of 60 s. (c) Variation of the formaldehyde outlet concentration as a function of the methanol inlet load.

methylotrophic yeast *P. pastoris*. The determination of the methanol removal profiles and formaldehyde generation show that the biomass present in the reactor is capable of degrading the formaldehyde generated as the concentration of methanol decreases. However, an increase in the methanol inlet load above the critical value can lead to the emission of formaldehyde into the environment.

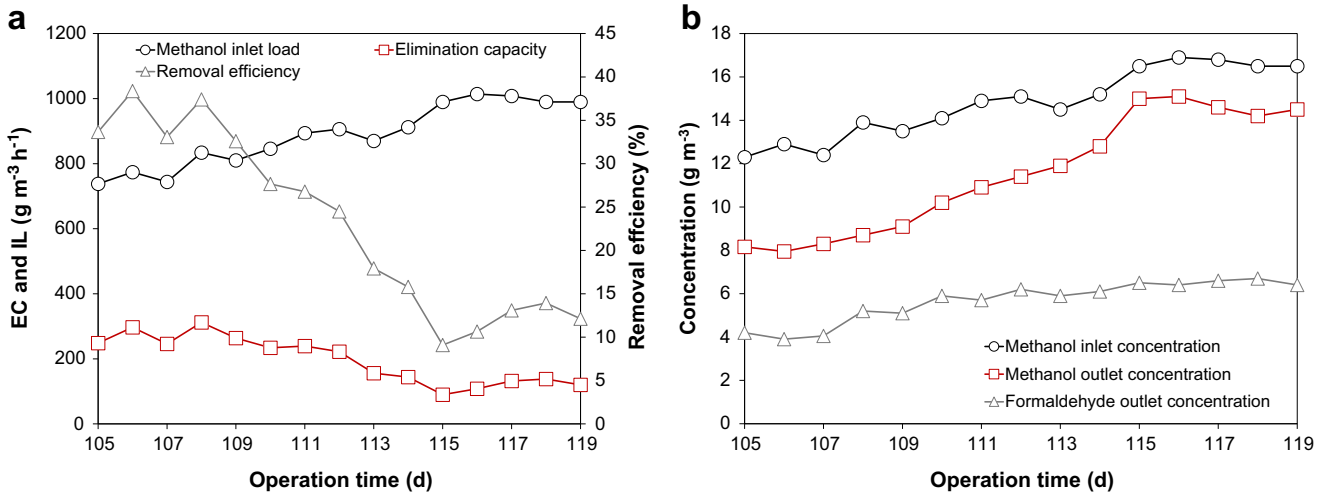

Fig. 5. (a) Variation of the methanol inlet load, elimination capacity and removal efficiency during the overload operation. (b) Variation of the inlet and outlet methanol concentration and formaldehyde outlet concentrations during the overload operation.

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