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Effect of trace gases, toluene and chlorobenzene, on methane biofiltration: An experimental study

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HIGHLIGHTS

- Methane biofiltration was studied in presence of either toluene or chlorobenzene.
- Inlet load of methane had an influence on methane elimination capacity.
- Both toluene and chlorobenzene decreased the elimination capacity of methane.

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ABSTRACT

Two trace gases, toluene and chlorobenzene, were added separately to a methane-treating biofilter using an inorganic filter material. At two fixed inlet loads of methane, 16 gC/(m^3 h) and 66 gC/(m^3 h), the influence of the concentration of toluene and chlorobenzene on methane removal was investigated. Constant elimination capacities of methane were achieved at the lowest inlet load of methane whatever the inlet load of toluene or chlorobenzene were, with 7.6 ± 0.4 gC/(m^3 h) for toluene-biofilter and 5.9 ± 0.4 gC/(m^3 h) for chlorobenzene-biofilter. Elimination capacities of methane were more affected by the trace gases for the highest inlet load of methane with a decrease from 13.6 ± 1.0 gC/(m^3 h) to 1.4 ± 0.5 gC/(m^3 h) for toluene-treating biofilter and from 11.1 ± 0.5 gC/(m^3 h) to 4.0 ± 0.6 gC/(m^3 h) for chlorobenzene-treating biofilter. A maximum elimination capacity of 49 gC/(m^3 h) for toluene was achieved for the lowest inlet load of methane while only 36 gC/(m^3 h) for toluene was reached for the highest inlet load of methane. A maximum elimination capacity of 2 gC/(m^3 h) of chlorobenzene was obtained for the two inlet loads of methane. This study shows that methane biofiltration may be disrupted by the presence of a trace gas in a long term operation depending on the inlet load of methane.

1. Introduction

The biodegradation of municipal stored wastes in anaerobic conditions in landfills is responsible for biogas generation. Biogas mainly consists of methane (CH_4) and carbon dioxide (CO_2) with concentrations of 50–60% v/v and 40–50% v/v respectively [1,2]. The biogas contribution to global warming is noteworthy as CH_4's global warming potential is 25 times that of CO_2 over a 100-year period [3]. In Canada, landfills contributed to 20% of CH_4 emissions in 2008 [4]. The landfill biogas composition was reported to contain more than 200 non-methane organic compounds (NMOC) which represents 1% of the total biogas volume [2]. Their origins may be imputed to intermediate biochemical reactions associated with degradation and volatilization processes of organic wastes disposed of in landfills [5,6]. The broad list of identified compounds has been divided into main families such as alkanes, alcohols, ketones, aromatics, chlorinated aliphatic hydrocarbons, chlorofluorocarbons, terpenes and siloxanes [2,6,7].

Biofiltration is a technology able to attenuate CH_4 emissions, particularly in small and old landfills, but also in large and new landfills as a post-treatment of energy recovery or flaring [8,9]. Biofiltration of CH_4 is well documented with regards to operational parameters such as temperature, bed moisture, properties of the packing material, supply of essential nutrients, inlet load, oxygen concentration and even extrapolymeric substance formation.

However, the complexity of the biogas mixture has underlined a new parameter: the presence of NMOCs. Recent studies have dealt with the cometabolic properties of methanotrophs, the CH_4-degrading bacteria, and the various interactions that may occur between the compounds and the microorganisms. Most of the experiments were carried out in batch experiments to assess the effect of different trace gases on the CH_4 bio-oxidation [10–13]. A few studies take into consideration dynamic factors in using a

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dynamic column set-up in addition to the batch experiments [14,15]. A wide range of trace gases have been investigated, from aromatic hydrocarbons (like benzene, toluene) to chlorofluorocarbons and hydrochlorofluorocarbons without forgetting chlorinated compounds (like trichloroethylene, vinyl chloride, dichloromethane and trichloroethane) [10–15].

The objective of this study was to investigate the effect of both toluene and monochlorobenzene as trace gas compounds on CH_4 biodegradation in a lab-scale column biofilter. The removal of the trace gases was also evaluated. Toluene was chosen because of its large distribution in landfill biogas [2,6] while monochlorobenzene was taken more particularly to represent an aromatic chlorinated compound more recalcitrant to the bio-oxidation than toluene [16].

2. Materials and methods

2.1. Experimental set-up

The experimental set-up is shown in Fig. 1. The upflow laboratory-scale biofilter column was made of Plexiglas with an internal diameter of 0.15 m. The biofilter was divided into three identical sections of 0.32 m high and was filled with a stone based inorganic medium. Due to confidential reasons, the nature of the packing material cannot be revealed. Some characteristic can be given as the equivalent diameter of 7.3 ± 0.2 mm, the specific surface area of 470 m^2/m^3 and a void space volume of 0.43 [17]. The gas mixture was fed to the bottom of the biofilter and consisted of mixing pre-humidified air, pure CH_4 (Praxair Inc., Québec) and vapors of toluene (Fisher Scientific 99.99%) or monochlorobenzene (Acrôs Organics 99%). The VOCs (volatile organic compounds) vapors were produced by flowing dry air through a saturation chamber. The air flow rates were regulated by mass flow controllers (Brooks, Series 0154 and 0254). The effluent gas was sent to an evacuation system.

2.2. Operating conditions

Experiments were carried out on four different biofilters to evaluate both the influence of the VOC on CH_4 elimination and the behavior of VOC degradation in presence of CH_4. The biofilters were all operated under the same inlet air flow rate of 0.25 m^3/h corresponding to an empty bed residence time (EBRT) of 250 s.

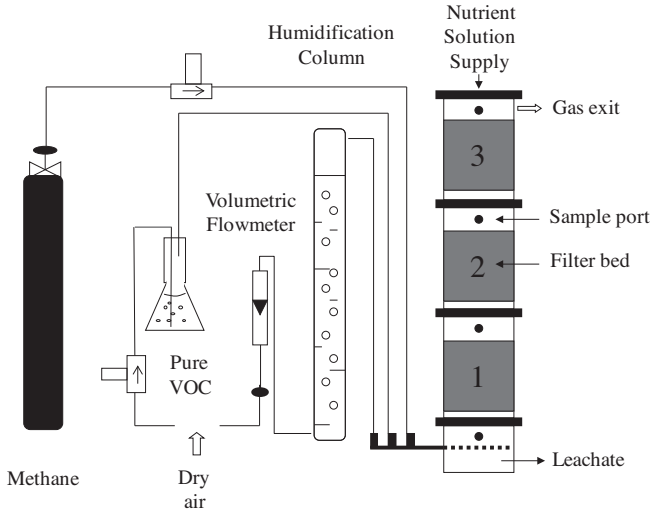

Fig. 1. Experimental set-up of the biofilter. The numbers 1, 2, 3 correspond to the stage number of the biofilter.

The experiment was carried out in two series: BT and BC for the biofilter operated with both CH_4 and either toluene (C_7H_8) or monochlorobenzene (C_6H_5Cl), respectively.

Two fixed concentrations of CH_4, (1): 1.0 gC/m^3 (2000 ppmv) and (2): 4.4 gC/m^3 (9000 ppmv), were studied. The numbers 1 and 2 are linked to the level of CH_4 concentration mentioned before. BT1 and BT2 were operated at four concentrations of toluene: 0.8, 1.7, 2.8 and 3.8 gC/m^3, and BC1 and BC2 at three concentrations of chlorobenzene: 0.08, 0.24 and 0.48 gC/m^3. The concentrations of toluene and chlorobenzene in this study were higher than those reported in landfills, varying from 3 to 2471 $\mu g/m^3$ [6,18–20] and from 0.01 to 2.2 $\mu g/m^3$ [19,20] respectively. Higher concentrations were chosen to accentuate the impact of trace gas compounds on methane biodegradation.

A nutrient solution (NS) was applied daily to each biofilter at a rate of 1.3 L/day. The detailed composition of the NS for macronutrients and micronutrients is shown in Table 1.

2.3. Analytical methods

Methane and VOCs concentrations were measured in the biofilter at the four sample ports using a total hydrocarbon analyzer (FIA-510, Horiba, USA), CO_2 concentrations were measured with a portable gas analyzer system (Ultramat 22P, Siemens AG, Germany). The measured CO_2 concentrations accounted for both the production of CO_2 by CH_4 and VOC oxidation. The concentrations of the VOC were determined by subtracting the concentration of CH_4 measured alone to the total hydrocarbon concentration analyzed originally.

The bed pressure drop was measured with a differential manometer (Type 4, Air Flow Developments Ltd., UK).

2.4. Parameters for analyzing biofilter performance

The performance of a biofilter is expressed in terms of the inlet load IL of the compound i ($g_i/(m^3\,h)$), the elimination capacity EC_i ($g_i/(m^3\,h)$), the removal efficiency RE_i (%), and the CO_2 production rate PCO_2 ($gCO_2/(m^3\,h)$) calculated as shown below:

$$IL_i = \frac{C_{i,in} * Q}{V_{bed}} \quad (1)$$

$$EC_i = \frac{(C_{i,in} - C_{i,out}) * Q}{V_{bed}} \quad (2)$$

$$RE_i = 100 * \frac{C_{i,in} - C_{i,out}}{C_{i,in}} \quad (3)$$

$$PCO_2 = \frac{(C_{CO_2,out} - C_{CO_2,in}) * Q}{V_{bed}} \quad (4)$$

where Q is the total air flow rate (m^3/h), V_{bed} is the packing bed volume (m^3), $C_{i,in}$ and $C_{i,out}$ are the inlet and the outlet concentration of

Table 1
Composition and concentration of the macronutrient and micronutrient solution.

Macronutrients	Concentration (mg/L)	Micronutrients	Concentration (μg/L)
$NaNO_3$	3038	$ZnSO_4$, $7H_2O$	576
K_2SO_4	170	$MnSO_4$, $7H_2O$	466
$MgSO_4$, $7H_2O$	37	H_3BO_3	124
$CaCl_2$, $2H_2O$	7	$NaMoO_4$, $2H_2O$	96
KH_2PO_4	530	$CoCl_2$, $6H_2O$	96
Na_2HPO_4	860	KI	166
		$CuSO_4$, $5H_2O$	250
		$FeSO_4$, $7H_2O$	112

the compound *i* respectively (gC/m^3), $C_{CO_2,in}$ and $C_{CO_2,out}$ are the CO_2 inlet and outlet concentration (gCO_2/m^3).

2.5. Microbial counting

The Most Probable Number (MPN) method employing 96-well microtiter plates was used to enumerate the total culturable microorganisms in the different sections of the biofilter. The biofilters were sampled when the performance of the biofilter were stabilized, generally around 15 days after each change of operating condition. Three replicates were taken for each section. For determination of microbial count, 10 g of humid packing were mixed in 20 mL of buffered solution containing 0.1% (w/v) sodium pyrophosphate and 2% (w/v) NaCl in sterile tubes. The tubes were then vortexed for 30 s at the maximum speed, laterally shaken for 30 min (250 rpm) and finally centrifuged for 2 min (1000 rpm) to separate major debris from the supernatant. The supernatant was appropriately diluted and plated on nutrient plates consisting of 0.5% (w/v) tryptone, 0.25% (w/v) yeast extract, and 0.1% (w/v) dextrose. The plates were incubated for 24 h at 28–30 °C. To reveal the positive wells, INT (an iodonitrotetrazolium violet solution) was added. Results were interpreted using a MPN calculation module, as described by Roy [21]. These experiments were carried out on the four biofilters BT1, BT2, BC1 and BC2 for C_7H_8 concentrations of 0.8 and 1.7 gC/m^3 and C_6H_5Cl concentrations of 0.08 and 0.24 gC/m^3.

3. Results and discussion

3.1. Effect of methane concentration

Fig. 2 presents the elimination capacity of both methane and toluene as a function of inlet load of toluene for the lowest and the highest methane inlet loads, BT1 and BT2 respectively. The results show that the concentration of methane influenced the behavior of the toluene on methane removal. At a low methane-IL of 16 gC/(m^3 h), no significant difference was observed in methane-EC which averaged 7.6 ± 0.4 gC/(m^3 h), for the whole toluene-IL tested from 0 to 46.5 gC/(m^3 h). An ANOVA test was performed to analyze the difference of means of methane-EC for each toluene-IL. The results of ANOVA test are presented in Table 2. For a confidence interval of 95%, there was no statistical difference of methane-EC for the lowest concentration of methane (BT1) whatever the inlet loads of the toluene (signification value

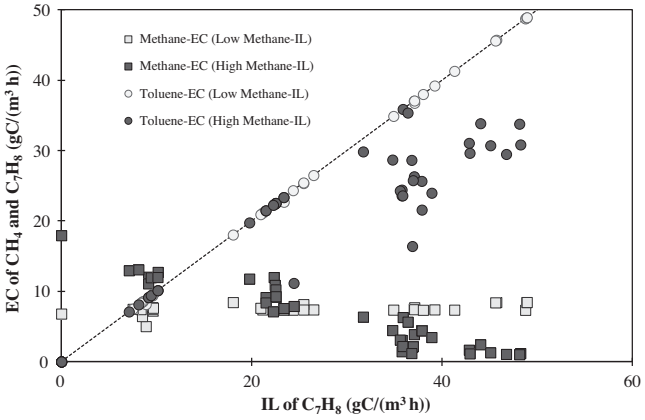

Fig. 2. Elimination capacity of both methane and toluene as a function of inlet load of toluene at methane inlet load of 16 gC/(m^3 h) (low-IL: light color) and 66 gC/(m^3 h) (high-IL: dark color). The dotted line represents the 100% elimination of toluene.

Table 2
Results of the multiple comparisons of methane-EC means as a function of the trace gases inlet load for BT1, BT2 and BC1, BC2.

BT1			BC1		
C_7H_8-IL	C_7H_8-IL	Signification[a]	C_6H_5Cl-IL	C_6H_5Cl-IL	Signification
0	36.3	0.370	0	3.3	1.000
	46.5	0.021		6.7	0.895
9	36.3	0.990	1.2	3.3	0.775
	46.5	0.127		6.7	0.237
BT2			BC2		
C_7H_8-IL	C_7H_8-IL	Signification	C_6H_5Cl-IL	C_6H_5Cl-IL	Signification
0	36.3	0.001	0	3.3	0.007
	46.5	0.014		6.7	0.001
9	36.3	0.000	1.2	3.3	0.026
	46.5	0.000		6.7	0.005

[a] The mean difference is significant at 0.05.

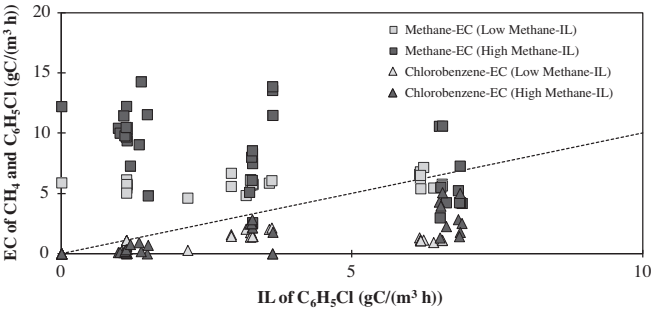

Fig. 3. Elimination capacity of both methane and chlorobenzene as a function of inlet load of chlorobenzene at methane inlet load of 16 gC/(m^3 h) (low-IL: light color) and 66 gC/(m^3 h) (high-IL: dark color). The dotted line represents the 100% elimination of chlorobenzene.

superior to 0.05). For the high methane-IL of 66 gC/(m^3 h), methane-EC was affected by the inlet load of toluene as methane-EC decreased from 18 to 1.4 gC/(m^3 h) with toluene-IL increasing from 0 to 46.5 gC/(m^3 h) (Fig. 2). For BT2, there were significant differences, for methane-EC corresponding to the two highest toluene-IL (36.3 gC/(m^3 h) and 46.5 gC/(m^3 h)) in comparison to the two lowest toluene-IL (0 gC/(m^3 h) and of 9 gC/(m^3 h)), with p-values below 0.05 (Table 2).

Fig. 3 is related to the chlorobenzene-treating biofilters, BC1 and BC2. The elimination capacity of both methane and chlorobenzene are presented as a function of inlet load of chlorobenzene for the lowest and the highest methane inlet loads. The methane-EC remained relatively constant at 5.9 ± 0.4 gC/(m^3 h) at methane-IL of 16 gC/(m^3 h) whatever the inlet load of chlorobenzene was, while the methane-EC decreased from 10.9 ± 1.2 gC/(m^3 h) to 4.7 ± 1.3 gC/(m^3 h) at the highest methane-IL of 66 gC/(m^3 h). The ANOVA test (Table 2) indicates that no significant difference was noticed for methane-EC for BC1 according to the chlorobenzene-IL (alpha value superior to 0.05). For BC2, the methane-ECs corresponding to the two highest chlorobenzene-IL (3.3 and 6.7 gC/(m^3 h)) were statistically different to the case without chlorobenzene and the chlorobenzene-IL of 1.2 gC/(m^3 h).

3.2. Effect of toluene on methane biofiltration profile

Fig. 4a and b presents the conversion of both toluene and methane for each stage of the biofilter as a function of toluene concentration for the lowest inlet load of methane of 16 gC/(m^3 h) (BT1).

In BT1, all the toluene was essentially removed in stages 1 (79 ± 3%) and 2 (20 ± 4%). A decrease of methane-RE was observed

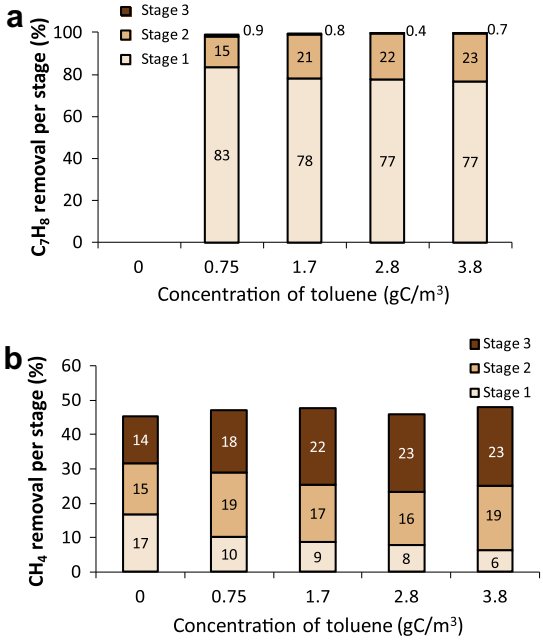

Fig. 4. Toluene (a) and methane (b) removal per stage as a function of toluene concentration for BT1.

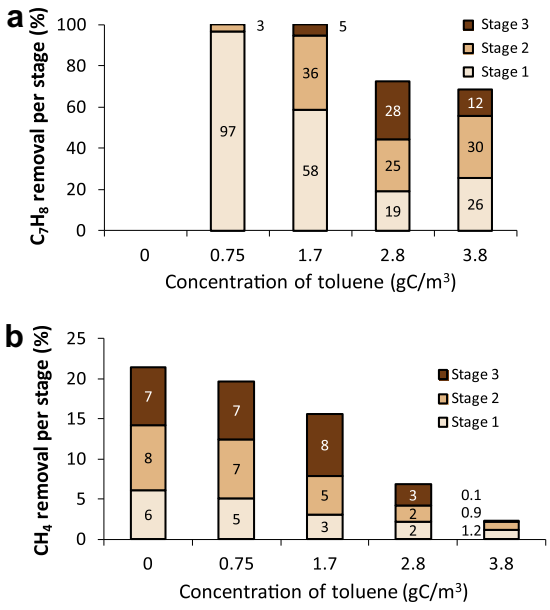

Fig. 5. Toluene (a) and methane (b) removal per stage as a function of toluene concentration for BT2.

in the stage 1, from 17 ± 4% to 6 ± 0.5% for toluene concentrations varying from 0 to 3.8 gC/m^3, respectively. The methane-REs were of 17 ± 2% and 21 ± 5% in average for all the toluene concentrations in stages 2 and 3 respectively.

The methane-RE decreased in stage 1 as the toluene-IL increased, because higher amount of toluene were removed. As all the toluene was degraded in stages 1 and 2, the methane-RE was nearly not affected in stage 3, which may explain the highest methane-RE in this specific stage. Whatever the microorganisms present in the biofilter, toluene is an easier substrate to degrade than methane as it has a higher solubility. For instance, the dimensionless Henry's constant is 0.27 for toluene and 30.2 for methane in water at 25 °C [22]. The comparison of Henry's constant is indicative of the solubility level of each compound in water as the lower the value is, the more soluble is the compound.

Fig. 5a and b shows the conversion of toluene and methane for each stage as a function of toluene concentration for BT2 (methane-IL = 66 gC/(m^3 h)). The effect of toluene concentration on methane removal was more pronounced in BT2 than in BT1. The total toluene-RE was of 100% for the lowest toluene concentrations of 0.75 and 1.7 gC/m^3 and decreased to 70% in average for the highest toluene concentrations of 2.8 and 3.8 gC/m^3 (Fig. 5a). While stage 1 removed most of the toluene, from 97% to 58%, at low concentrations of 0.75 and 1.7 gC/m^3, the toluene removal was more equally divided between the stages at high toluene concentrations, with an average toluene-RE of 23 ± 7% per stage. As observed in Fig. 5b, each stage removed in average 7 ± 1% of methane in the absence of toluene for a total conversion of 21%, and no more than 2% of methane was removed for each stage for the highest toluene concentration of 3.8 gC/m^3 meaning that at high IL of toluene, methane biodegradation was inhibited. As a first hypothesis, the mass transfer of both compounds from gas to biofilm should be significantly reduced particularly due to the accumulation of biomass, suggested by the increase of pressure drop ranging from 0.55 to 3.95 cmH_2O/m from day 48 to day 66 (Table 4). Another hypothesis could be the presence of by-products of toluene degradation which could generate toxicity towards methane oxidation. A previous study of methane biodegradation in presence of other compounds such as benzene and toluene has led to the conclusion of the presence of toxicities towards methane oxidation from catechol and phenol, the biotransformation products of benzene and toluene respectively [23].

The influence of aromatic compounds on methane biodegradation had been the subject of some studies in relation to the context of landfill biogas [24]. The ratio methane-IL (7.7 gC/(m^3 h)): trace gas compound-IL, either toluene-IL (0.01 gC/(m^3 h)) or benzene-IL (0.03 gC/(m^3 h)), had no significant effect on methane oxidation [15]. The methane-RE was of 77 ± 6%, which corresponded to a methane-EC of 5.8 gC/(m^3 h). In batch experiments, benzene was found to have toxic effects on methane oxidation, at concentration above 0.04 gC/m^3, for a methane concentration of 24.2 gC/m^3 [24]. The range of concentration ratios, from 280 to 770 gC–CH_4/gC-trace gas compound, were much wider than those encountered in the present study, from 0.3 to 7.3 gC–CH_4/gC–C_7H_8 for toluene biofilter experiments. The inhibition effect of toluene on methane biodegradation at high inlet loads may be overestimated in the context of elimination of landfill biogas as toluene concentration should be lower.

3.3. Effect of chlorobenzene on methane biofiltration profile

Fig. 6a and b presents the conversion of chlorobenzene and methane for each stage as a function of chlorobenzene concentration for BC1 (methane-IL = 16 gC/(m^3 h)) while Fig. 7a and b presents the conversion of chlorobenzene and methane for BC2 (methane-IL = 66 gC/(m^3 h)). It should be mentioned that a lag phase from 7 to 20 days occurred both in BC1 and BC2 for chlorobenzene biodegradation. The values of conversion, presented in the following sections for BC1 and BC2 are the average of both chlorobenzene and methane conversion when the chlorobenzene degradation was stabilized during around 9 days for each concentration.

In BC1, the lag phase occurred in stage 1 for 7 days at 0.08 gC/m^3 of chlorobenzene. When the chlorobenzene degradation was stabilized, the conversion of chlorobenzene reached 65 ± 1% in stage 1, 29 ± 1% in stage 2 and 7 ± 1% in stage 3 (Fig. 6a). At 0.24 gC/m^3 of chlorobenzene, the conversion decreased and stabilized at 12 ± 3% in stage 1, at 20 ± 3% in stage 2 and 11 ± 0% in stage 3. Finally, at 0.48 gC/m^3, the conversion decreased to reach constant value of 0%, 11 ± 1% and 6 ± 1% in stages 1, 2 and 3 respec-

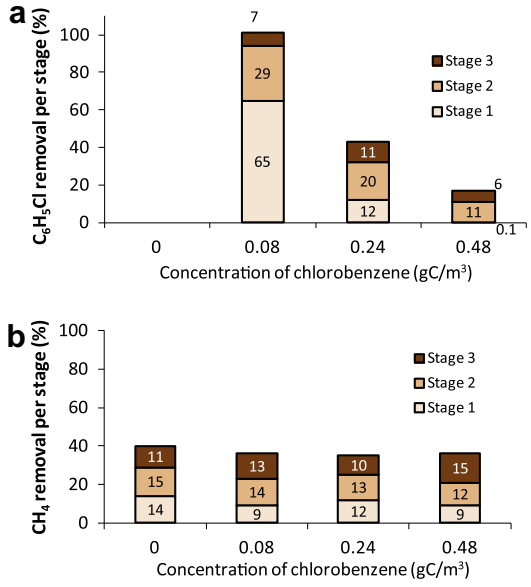

Fig. 6. Chlorobenzene (a) and methane (b) removal per stage as a function of chlorobenzene concentration for BC1.

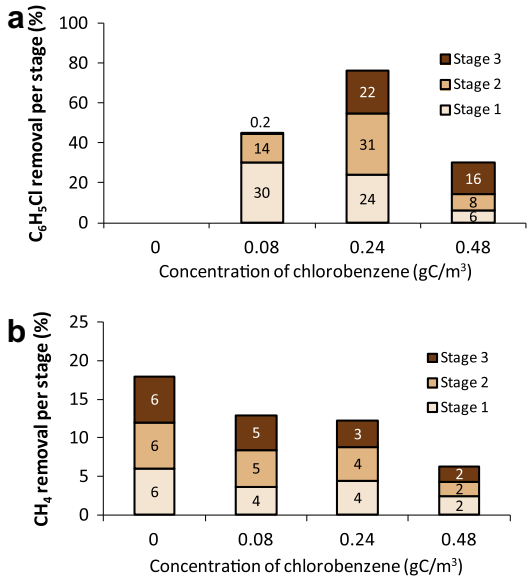

Fig. 7. Chlorobenzene (a) and methane (b) removal per stage as a function of chlorobenzene concentration for BC2.

tively. Meanwhile, the degradation profile of methane was relatively constant when the concentrations of chlorobenzene varied from 0.08 to 0.48 gC/m^3. The three stages removed in average 12 ± 2% of methane (Fig. 6b).

After 21 days at 0.08 gC/m^3 of chlorobenzene in BC2, stage 1 removed 30% of chlorobenzene, stage 2, 14% and stage 3, 0.2% for a total-RE of 44% (Fig. 7a). The global chlorobenzene-RE increased to 77% for 0.24 gC/m^3 of chlorobenzene (24%, 31% and 22% of conversion in average in stages 1, 2 and 3), and decreased to 30% for the highest chlorobenzene concentration of 0.48 gC/m^3 (6%, 8% and 16% of chlorobenzene-RE for each stage). Concerning methane, the initial removal of methane without chlorobenzene was 6 ± 0.5% for each stage and decreased progressively with the increasing chlorobenzene concentration. For the highest concentration of chlorobenzene of 0.48 gC/m^3, only 2 ± 0.5% of methane was removed from each stage for a total conversion of 6% (Fig. 7b).

Two main assumptions should be considered concerning the degradation of chlorobenzene. The cometabolism properties of methane-oxidizing bacteria could result in both the degradation of chlorobenzene and methane. Indeed, methanotrophic bacteria are well known to co-oxidize various halogenated compounds, most particularly trichloroethylene [25–27] but inhibition may occur from the presence of cometabolic substrates and chlorinated compound product toxicity [28]. To our knowledge, there is no report in the literature of simultaneous biofiltration of methane and chlorobenzene. However, the biofiltration of methane in presence of a chlorinated compound like trichloroethylene, dichloromethane or vinyl chloride was more widely studied than aromatics [11,13,15,24]. In these previous studies, the biodegradation of methane was negatively impacted. Competitive and uncompetitive inhibitions were found to describe the behavior of dichloromethane and trichloroethylene on methane removal [13,24] while vinyl chloride may present toxic effect [15]. In batch experiments, for an initial methane concentration of 24.2 gC/m^3, concentration of 0.011 gC/m^3 of trichloroethylene and 0.006 gC/m^3 of dichloromethane decreased the methane oxidation rate of 80% and 90% respectively, in comparison to methane alone [24]. In column experiment, the ratio methane-IL (7.7 gC/(m^3 h)): vinyl chloride-IL (0.004 gC/(m^3 h)) had a significant effect on methane oxidation [15]. The methane-RE was of 35 ± 3%, which corresponded to a methane-EC of 2.7 gC/(m^3 h). The range of concentration ratios, from 2000 to 4400 gC–CH_4/gC-chlorinated compound, were also wider than those encountered in the present study, from 2 to 54 gC–CH_4/gC–C_6H_5Cl for chlorobenzene biofilter experiments. Secondly, the development of specific chlorobenzene-degrading bacteria should not be forgotten. The presence of lag phase in certain stages, as stage 1 for example, may support this assumption.

As noticed by Delhoménie and Heitz [16], there is an influence of the presence of a halogen atom on the aromatic ring which tends to disturb the microbial degrading activity. This may explain the different behaviors observed between the two trace gas compounds, toluene and chlorobenzene. Inlet loads of toluene were broadly higher than the ones for chlorobenzene, and the elimination capacity were distinctly superior for the methylated aromatic compound (46.5 gC/(m^3 h) for BT1 and 31.3 gC/(m^3 h) for BT2) than the halogenated aromatic compound (2 gC/(m^3 h) for BC1 and BC2).

3.4. Carbon dioxide production

According to the stoechiometric reactions considering that biomass is not generated, the mass-ratio of CO_2 produced to the amount of either methane, toluene or chlorobenzene degraded should be 2.75, 3.34 and 2.35 respectively for complete oxidation of these pollutants to CO_2 and water (H_2O).

When biomass is taken into account, the stoechiometric reactions (the biomass formula was chosen as $C_5H_7NO_2$, [29]) are as follows:

$$aCH_4 + bO_2 + cNaNO_3 \rightarrow C_5H_7NO_2 + dH_2O + eCO_2 + \text{salts} \quad (5)$$

$$a_1C_7H_8 + b_1O_2 + c_1NaNO_3 \rightarrow C_5H_7NO_2 + d_1H_2O + e_1CO_2 + \text{salts} \quad (6)$$

$$a_2C_6H_5Cl + b_2O_2 + c_2NaNO_3 \rightarrow C_5H_7NO_2 + d_2H_2O + e_2CO_2 + f_2HCl + \text{salts} \quad (7)$$

The experimental mass ratio of PCO_2/total EC is defined as the carbon dioxide yield coefficient (YCO_2). Table 3a presents the results obtained from the linear regression of PCO_2 as a function of the total EC ($C_7H_8 + CH_4$) for BT1 and BT2; Table 3b presents YCO_2 for BC1 and BC2 as a function of the total EC ($C_6H_5Cl + CH_4$).

Table 3
Results of the linear regression of PCO_2 as a function of total EC for (a) BT1, BT2 and (b) BC1, BC2.

(a) Toluene			(b) Chlorobenzene		
Biofilter	YCO_2	r^2	Biofilter	YCO_2	r^2
BT1	2.40	0.96	BC1	1.70	0.41
BT2	3.03	0.85	BC2	2.17	0.68

The variation of PCO_2 as a function of total EC was linear in the case of the mixture of toluene and methane (r^2 of 0.96 and 0.85 for BT1 and BT2). The values of YCO_2 varied from 2.40 to 3.03 gCO_2/gC for BT1 and BT2 respectively for toluene-IL ranging from 0 to 46.5 $gC/(m^3\ h)$. The difference between BT1 and BT2 lies in the amount of carbon removed. A higher ratio was obtained for BT2 as both PCO_2 and total EC reached a plateau (93 $gCO_2/(m^3\ h)$ and 31 $gC/(m^3\ h)$ respectively) for toluene-IL varying from 23.1 to 46.5 $gC/(m^3\ h)$, while for BT1, a linear increase of PCO_2 and total EC were noticed. The values of YCO_2 obtained in the present study are in the range of those reported by Gallastegui et al. [17] (YCO_2 of 2.41 gCO_2/gC for toluene removal in an inorganic biofilter). Monitoring CO_2 production is useful to determine the level of mineralization of toluene and methane. However, the amount of CO_2 produced by each compound was not determined in the present study.

For the mixture of methane and chlorobenzene, a mineralization of the compounds was noticed as the values of YCO_2 varied from 1.70 to 2.20 gCO_2/gC for BC1 and BC2 (Table 3b). However, r^2 values were as low as 0.41 and 0.68 for BC1 and BC2.

For BC1, the pH of the leachate dropped from 8.05 ± 0.03 at day 19 to 7.14 ± 0.14 at day 44 while it was at 8.21 ± 0.06 for the nutrient solution. A similar trend was noticed for BC2, the pH of the leachate decreased from 8.35 ± 0.15 at day 2 to 6.93 ± 0.04 at day 32. This pH variation may support the assumption that there was the loss of the chlorine atom of chlorobenzene forming hydrochloric acid (HCl).

3.5. Evolution of the pressure drop

The pressure drop (ΔP), measured at the beginning and at the end of each experiment, are presented in Table 4 as the initial – final values. Pressure drop of BT1 never exceeded 0.03 cmH_2O/m while the toluene concentration was varied from 0.8 to 3.8 gC/m^3. Nematodes were noticed in stages 1 and 2 of the biofilter. The nematodes are known for their ability to reduce the excess of microbial biomass accumulation and have even been reported in toluene-treating biofilter [30,31]. The low ΔP was consistent with the high toluene conversion rate observed during all the experimentations. Previous experiment with a toluene-treating biofilter reported that ΔP may have an impact on toluene removal efficiencies [32]. Therefore, bed-water washing was carried out by the authors to prevent the formation of excessive biomass.

Table 4
Initial and final pressure drop of the biofilters.

Biofilter	Period (days)	$[C_7H_8]$ (gC/m^3)	Pressure drop (cmH_2O/m)
BT1	1–20	0.8–3.8	0.01–0.03
BT2	7–26	0.8	0.08–0.14
	27–47	1.7	0.15–0.50
	48–66	2.8	0.55–3.95
	184–209	3.8	0.09–0.27
		$[C_6H_5Cl]$ (gC/m^3)	
BC1	19–107	0.08–0.48	0.05–0.07
BC2	2–147	0.08–0.48	0.05–0.09

In BT2, high ΔP were noticed when the toluene concentration increased from 0.8 to 3.8 gC/m^3. The ΔP slowly increased from 0.08 to 0.14 cmH_2O/m and from 0.15 to 0.50 cmH_2O/m for 0.8 and 1.7 gC/m^3 of toluene concentration respectively. However, the ΔP of BT2 increased as high as 3.95 cmH_2O/m for toluene concentration of 2.8 gC/m^3. A backwash decreased the ΔP to 0.09–0.27 cmH_2O/m for the last toluene concentration tested of 3.8 gC/m^3. The presence of ΔP as high as 3.95 cmH_2O/m at 2.8 gC/m^3 of toluene induced a reduction of the toluene removal of 28% from the toluene concentration of 1.7 gC/m^3 and therefore a reduction of the methane removal of 56%. Several factors may explain the occurrence of high ΔP, such as the characteristics of packing material and the formation of excessive biomass [33].

The high ΔP in BT2 may be explained by the fact that at high inlet concentrations of pollutants, there was an increase of both cell growth rate and biomass accumulation which led to higher biofilm thickness and therefore higher ΔP [34]. It should be noticed, however, that toluene-treating biofilter are known to be affected by the formation of excessive amounts of biomass and to undergo a decrease in pollutant removal as the ΔP increases [34–36].

The ΔP of BC1 and BC2 remained as low as 0.09 cmH_2O/m during all the experiments (Table 4). No visible biomass was observed in the filter beds. This is coherent with the study of Wang et al. [37], where a biomass accumulation of 0.059 kg was obtained after 213 days of biofilter operation. The authors assumed that this relatively low biomass accumulation was due to the low inlet organic loading of chlorobenzene which varied from 8 to 57 $gC/(m^3\ h)$. However, it contrasts with the study of Delhoménie and Heitz [16] where a visible dark biofilm was observed and the calculated biomass yield coefficient was 0.2 g biomass produced/g chlorobenzene removed for a chlorobenzene-IL varied up to 122 $gC/(m^3\ h)$, much higher than the one used in this study.

3.6. Effect of trace gas compounds on microbial population

Fig. 8 presents the log of the average colony forming units (CFU) per gram of the wet weight of the packing material as a function of the total inlet carbon concentration for both the toluene and chlorobenzene-treating biofilters. A decrease of the CFU was noticed in the case of the toluene biofilter as the total inlet concentration increased from 1.1 to 6.0 gC/m^3 while it remained constant for the chlorobenzene biofilter. High concentrations of pollutants may result in a decrease of the bacterial density as reported by Alvarez-Hornos et al. [38], in a toluene-treating biofilter. Concerning the chlorobenzene-treating biofilter, the CFU development seems to be limited, most probably due to the characteristic of the not-easily biodegradable chlorobenzene and not by the increase of the inlet carbon concentration.

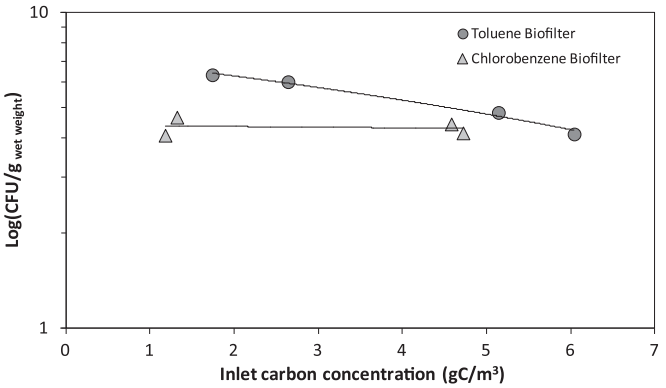

Fig. 8. Logarithm of the average Colony Forming Unit of the entire biofilter as a function of the inlet carbon concentration for the toluene-treating biofilter (circle) and the chlorobenzene-treating biofilter (triangle).

Table 5
Total microbial count for each stage and the corresponding conversion (X) of toluene, chlorobenzene and methane per stage for BT1, BT2 and BC1, BC2.

	$[C_7H_8]$ = 0.8 gC/m^3			$[C_7H_8]$ = 1.7 gC/m^3		
	Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 3
BT1						
MPN[a] (CFU/g)	6.24×10^6	2.03×10^5	1.20×10^5	1.75×10^6	1.26×10^6	1.97×10^5
X C_7H_8 (%)	83	15	1	78	21	1
X CH_4 (%)	10	19	18	9	17	22
BT2						
MPN (CFU/g)	1.71×10^5	5.05×10^3	2.12×10^4	1.78×10^4	1.08×10^4	1.07×10^4
X C_7H_8 (%)	97	3	0	58	36	5
X CH_4 (%)	5	7	7	3	5	8
	$[C_6H_5Cl]$ = 0.08 gC/m^3			$[C_6H_5Cl]$ = 0.24 gC/m^3		
BC1						
MPN (CFU/g)	1.26×10^4	1.67×10^4	6.87×10^3	9.27×10^4	2.88×10^4	1.39×10^4
X C_6H_5Cl (%)	65	29	7	12	20	11
X CH_4 (%)	9	14	13	11	13	12
BC2						
MPN (CFU/g)	2.43×10^4	1.42×10^4	4.22×10^4	1.86×10^4	1.19×10^4	1.19×10^4
X C_6H_5Cl (%)	30	14	0.2	24	31	22
X CH_4 (%)	3.7	4.7	4.5	4.4	4.4	3.4

[a] MPN: Most Probable Number.

The comparison of the degradation profile of toluene and methane per stage to the total microbial count (MPN) for each section is presented in Table 5. In the case of toluene-treating biofilter, the highest MPN always occurred in stage 1, from 1.75×10^6 to 6.24×10^6 CFU/$g_{wet\ weight}$ for BT1 at 1.7 and 0.8 gC/m^3 of toluene respectively. For BT2, the MPN varied from 1.78×10^4 to 1.71×10^5 CFU/$g_{wet\ weight}$ for all the toluene concentrations tested. Meanwhile, the conversion of toluene in stage 1 was the highest, from 78% to 83% for BT1, and from 58% to 97% for BT2. The variation of MPN is less pronounced in stages 2 and 3. No relationship is noticeable between the conversion of methane and MPN for each section.

Concerning the chlorobenzene-treating biofilter, the MPN of each section remained in the same order of magnitude varying from 6.87×10^3 to 9.27×10^4 CFU/$g_{wet\ weight}$. No relation between the degradation of chlorobenzene or methane and the microbial density was observed.

4. Conclusion

Chlorobenzene and toluene were added separately as trace gases to methane-treating upflow biofilters, for inlet loads of methane of 16 and 66 gC/(m^3 h). The conversion of methane were not changed by the trace gas for the lowest inlet load of methane while the methane conversion rate dropped from 22% to 2% for the toluene-treating biofilter and from 17% to 6% for the chlorobenzene-treating biofilter for the highest inlet load of methane. The analysis of biodegradation profile for each compound showed that toluene was removed in priority in both the bottom and middle sections, thereby limiting the degradation of methane in the same sections. The occurrence of high pressure drop in the toluene biofilter with the highest inlet load of methane was correlated with the decrease of both methane and toluene elimination performance for the highest inlet loads of toluene. No pressure drop occurred in the chlorobenzene-treating biofilter, but the elimination performance of chlorobenzene was low. The toluene biofilter with the low methane-IL of 16 gC/(m^3 h) (BT1) obtained the best results in comparison to the other toluene biofilter with the high methane-IL of 66 gC/(m^3 h) (BT2) and both chlorobenzene biofilters (BC1 and BC2). The average colony forming units of BT1 was 98% superior to the average of the three other biofilters.

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