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A B S T R A C T

Continuously seeking the improvement of environmental protection, the limitation of exhaust emissions is of significance for the tire manufacturing industry. The aim of this study is to assess the potential of biofiltration for the treatment of such gaseous emissions. This work highlights that biofiltration is able to remove both hydrophilic and hydrophobic compounds within a single pilot unit of biofiltration. Due to Ethanol/Alkanes ratios (95/5 and 80/20), high performance levels were observed for low EBRT (16 and 12 s). After twenty days of stable running, the dynamic of stratification patterns could be explained as a result of species coexistence mechanisms. While its impact on performance has not been observed under stable operating conditions, the use of an adsorbent support such as granular activated carbon (GAC) could be relevant to promote system stability in the face of further perturbations, such as transient regimes, that are problematic in full-scale industrial applications.

Keywords:
Tire manufacturing industry
Biofiltration
Hydrophilic and hydrophobic compounds removal
Bioprocess understanding

1. Introduction

Sustainability is now part of engineering and manufacturing by taking into consideration key objectives such as competitiveness, profit and yield. Different authors (Rosen and Kishawy, 2012) highlight that, among industrial societies, the link between manufacturing processes and natural surroundings is now considered as a crucial factor in the decision making.

Along with the worldwide increased need of tyres with an annual manufacturing of about 1.4 billion products (Sienkiewicz et al., 2012), ongoing modifications in the tyre production process resulted in a substantive improvement of both protection of workers and limitation of the environmental impacts. According to the European Union Concerted Action EXASRUB database (de Vocht et al., 2008; Boniol et al., 2016) individual exposures to rubber gaseous emissions and inhalable dust has regularly decreased since the 1970s (around 4% per year). It has been suggested that this reduction is mainly due to technological improvement ways, modernisation of ventilation and extraction equipment and changes in working practices. As an example, the evaluation of the environmental impact of the gaseous emissions from the rubber manufacturing by the Swedish Environmental Protection Agency in 1991 revealed that the cessation of chemicals use or the replacement of chemicals that are harmful to human health and environment by safer ones are part of a global approach which aims for improvements in the production process (Forrest, 2015). However it is important that besides the efforts towards safer workplaces, technologies are also developed and implemented to control the emissions to the environment in particular stack exhaust emissions (Rosen and Kishawy, 2012), where it is common to find mixtures of biodegradable (such as alcohols) and more recalcitrant (mixtures of alkanes) Volatile Organic Compounds (VOCs). The composition of theses exhaust gases can vary from site to site depending on the chemicals being used in the processes and from country to country depending on the regulations in place.

The reduction of the environmental impacts of gaseous emissions is still topical and different studies are currently being conducted into the development of ever more effective and more technologically advanced treatment processes. It has been highlighted that biological technologies including biofilters, biotrickling filters, and bioscrubbers have been increasingly used due to their robustness, sensible cost-effectiveness and low environmental impact (Devinny et al., 1999; Datta and Grant Allen, 2005; Malhautier et al., 2005). In industrial applications, operating parameters of biofilters and biotrickling filters can be adapted to

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hydrophilic or lipophilic characteristics of the waste gas compounds (Pérez et al., 2015; San-Valero et al., 2018). Gas velocity within a biotrickling filter column could be 3–6 higher than for biofilter column, thus resulting in relatively small footprint. Even if a few works focus on evaluating clogging preventing methods (Nukunya et al., 2005; Dobslaw et al., 2018), this more compact design generally leads to higher specific loads, which may induce biofilm overgrowth and clogging (Revah and Morgan-Sagastume, 2005; Dobslaw and Ortlinghaus, 2020). Hence, in this work, biofiltration has been used as both high surface and low water content of biofilters make them more appropriate for the treatment of the less hydrophilic pollutants in the VOCs mixture to be treated. In a biofiltration configuration, off-gas emissions pass through a packed bed of humidified porous material supporting microorganisms as a biofilm. Biofilters are designed to allow physicochemical mass transfer of pollutants from the gas to the biofilm (liquid phase) which is responsible for pollutant oxidation (Malhautier et al., 2005). However, in some industrial applications, large footprint is needed for the treatment of less biodegradable VOCs for which the expected removal performance may not be achieved. Then, with increasing complexity of waste gas situations and tougher environmental regulatory constraints, multi-stage processes such as combinations of (non-)biological / biological processes are often required to yield performance expectations. Some applications may need physical/chemical pre-conditioning steps to achieve expected performance at short contact time such as around 10 s. Potential technologies such as UV oxidation (Kim et al., 2005; Zeng et al., 2016), non-thermal plasma (Dobslaw et al., 2017), electrostatic systems (Quan et al., 2017) could be used to achieve a partial oxidation of waste gas compounds (recalcitrant) to make the biodegradation easier. Technologies like adsorption could also be used to reduce the pollutants concentration variations at the biofilter inlet and different materials such as activated carbon (Aizpuru et al., 2003), and more recently biochars from different agricultural residuals (Hwang et al., 2018) and zeolite adsorber materials (Dobslaw et al., 2017) could be used. Moreover, these combinations.

The simultaneous elimination of VOC mixtures, representing different chemical groups by using biological ways has been thoroughly investigated by different authors for decades (Aizpuru et al., 2003; Cabrol et al., 2012; Yoshikawa et al., 2017; Dobslaw et al., 2019) as it is a challenging issue for industrial applications and special attention is required for hydrophobic VOCs removal (Cheng et al., 2016). The performance in biological treatment of different VOCs mixture containing both hydrophilic and lipophilic compounds has been determined. A vertical gradient of biodegradation activities which may be referred to a diauxic behaviour has been observed with the elimination of hydrophilic compounds before lipophilic compounds are metabolized (Khammar et al., 2005; Zehraoui et al., 2012). In this context, compound lipophilicity is a key parameter for microbial biodegradation as water solubility and, thus, substrate availability lowers with increasing lipophilicity (Dobslaw and Ortlinghaus, 2020). Another criterium is the molecular structure of compound. Even hydrophilic compounds might exhibit low elimination efficacy due to high steric hindrance towards enzymatic degradation (Dobslaw et al., 2019). Further systematic investigations will then be required to gain insight into substrate interaction mechanisms as knowledge concerning mutual effects on the metabolic process is still fragmented (Yang et al., 2018).

Finally, at industrial scale, a constantly operating biofiltration system is submitted to changing conditions (production shutdown periods, operational failures) that can impair their functional performance (Cabrol and Malhautier, 2011). It is then essential to identify these operating conditions (disturbance) that can reduce biofiltration performance, and to determine the capacity of the bioreactor to withstand a disturbance and to recover after disturbance. From these works, strategies to alleviate negative interactions among multiple VOCs will make it possible to promote full scale implementation of biofilters to multiple VOC removal (Yang et al., 2018).

The aim of this work is then to assess the potential of biofiltration for the treatment of gaseous emissions in the tire industry. The impact of gas velocity on the removal of chemicals will be firstly examined by using two pilot units fed with a synthetic mixture of biodegradable and hydrophobic compounds which is representative of on-site gaseous emissions. Then, the use of an adsorbent material (GAC) to improve biodegradation of alkanes will be examined.

2. Material and methods

2.1. Experimental design

Two identical polyvinyl chloride biofiltration columns entitled BF1 (BioFilter 1) and BF2 (BioFilter 2) (0.3 m internal diameter, 3.80 m height) were packed with sawmill wood chips (Table 1) to a height of 2 m. The bed height was subdivided into four compartments of 45–50 cm-height of material (Fig. 1). At the bottom of each column, a 10-cm Hiflow® rings layer was designed to homogenize the gas velocities before entering the organic material bed.

Gas-sampling ports were distributed at 0, 50, 105, 155 and 200 cm from the gas inlet. Gas-sampling ports were located in the 5-cm Hiflow® rings layers at the inlet and outlet of each compartment. On day 90, for BF1, the packing of the section near the gas outlet was removed and replaced by granular activated carbon (Table 1). For BF2, the packing of the section near the gas outlet was removed and replaced by a non-adsorbent synthetic packing material (confidential data) which was supplied by “" Manufacture Française des Pneumatiques Michelin ". This controlled package is comparable to GAC in terms of size.

Before both columns were filled with the material support, sawmill wood chips were seeded by dipping in activated sludge collected at a municipal wastewater treatment plant for one day. Granular Activated Carbon (GAC) and the non-adsorbent synthetic packing material have not been inoculated.

The packing material was regularly sprayed (four times a day) by a nutrient solution (Table 2) (agricultural fertilizer Optiplan, Duclos International, Lunel, France) according to a ratio carbon to total nitrogen 100/10 and corresponding to an average water supply of 15 L m^{-2} area day^{-1}, to maintain constant high moisture content and to provide essential nutrients for microbial growth (Khammar et al., 2005). The liquid medium did not provide any carbon as the only available carbon source was provided by the gas phase. pH of percolate waters was daily checked.

2.2. Inlet gas stream

BF1 and BF2 columns were run for more than 5 months, at ambient temperature, in an upward flow mode. Both biofilters were continuously fed by a synthetic gaseous effluent composed of a mixture of ethanol (VWR International France, Fontenay-sous-Bois, France) and solvent F (Essence F Onyx, Ardéa, Saint-Denis, France) mainly containing octane and methyl cyclohexane. Solvent F was designed as Alkanes along the entire manuscript. This gaseous effluent was representative of tire manufacturing emissions. This synthetic gaseous effluent was firstly saturated with moisture by using a downstream water scrubber before

Table 1
Main physico-chemical characteristics of used packing materials.

Measured parameters	Sawmill wood chips	Granular activated carbon
Mean diameter (mm)	13.1 ± 0.1	2.8 ± 0.1
Porosity of humid material (%)	60.4 ± 0.3	40 ± 5
Bulk density(kg m^{-3})	203 ± 25	558 ± 30
Specific surface area (m^2 m^{-3})	269 ± 12	2150 ± 57
Water-holding capacity (m^3 H_2O m^{-3} material)	0.20 ± 0.03	0.30 ± 0.02
pH	6.0 ± 0.0	7.8 ± 0.1

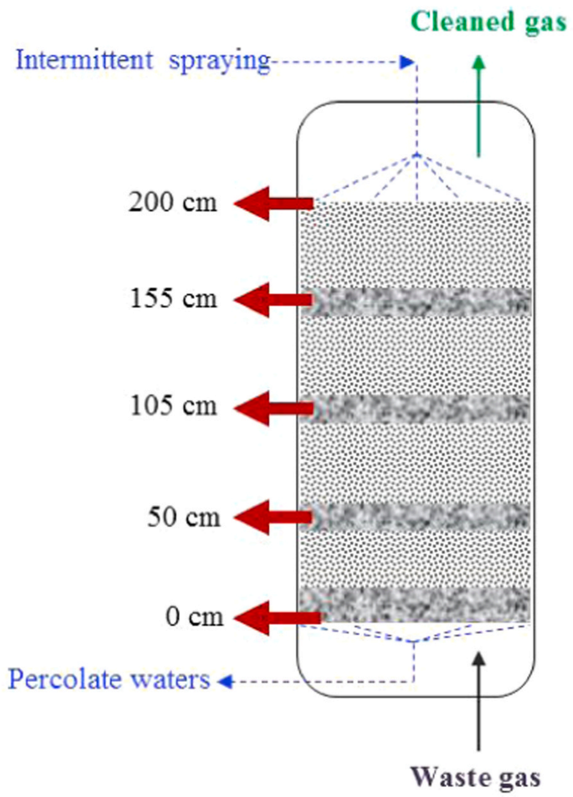

Fig. 1. Schematic representation of a pilot-scale biofiltration unit. [Hiflow® rings symbol] Hiflow® rings, [Sawmill wood chips symbol] Sawmill wood chips.

Table 2
Composition of the nutrient solution (agricultural fertilizer Optiplan, Duclos International, Lunel, France).

Compound	Mass percent fraction (%)
Nitrate	10
Ammoniacal nitrogen	12.2
Urea	1.8
Phosphoric anhydride	20
Potassium oxide	2
Magnesium oxide	2
Sulphur trioxide	4
Boron	0.0125
Copper	0.0025
Manganese	0.0125
Molybdenum	0.0012
Zinc	0.010
Iron	0.03

being treated by biofiltration.

Operating conditions of both biofilters are given on Table 3. The ratio Ethanol/Alkanes was of 95/5 or 80/20. Different Empty Bed Retention Time (EBRT) was tested: 36, 16 and 12 s for BF1; 21 and 12 s for BF2. Due to the size of the reactors, the complexity of the experimental device and the operation costs, the impact of EBRT has been evaluated in this way. VOCs levels increased from 121 ± 10–336 ± 67 mg carbon m^{-3} air. The dynamic generation system allowed to maintain stable VOCs target concentrations ranging from 10% to 20% of the mean value. All the graphs in the section Results and discussion were obtained from operating data (Fig. 1 on Supplementary Materials) collected during each stable period (Table 3).

2.3. *Sampling strategy and gas composition assessment*

Gaseous effluent was sampled at the different biofilter bed heights by using 10 L Nalophan® bags and a KNFN86KN pump (Midisciences, Rousset, France).

Total hydrocarbons levels have been measured daily by using a VOC analyzer equipped with a flame ionization detector (CHROMATHC, Chromatotec® group, France) according to the specifications of the manufacturer. A calibration curve has been prepared with external standards of ethanol.

Gaseous concentrations of ethanol and alkanes were quantified by using a gas chromatograph (Trace, Thermo Electron, France). The chromatograph was equipped with a gas sampling valve (at a temperature of 160 °C) which was connected to an apolar capillary column (Equity-1 Supelco, 30 m, 0.32 mm internal diameter, 0.25 mm film thickness) with a carrier gas (helium 5.0) at a flow rate of 1 mL min^{-1} and a flame ionization detector. The temperature of the detector was 220 °C. The analytical method consisted of three steps: firstly 40 °C for 1 min; then 10 °C min^{-1} from 40° to 100 °C; finally, 100 °C for 1 min. A calibration curve was prepared with external standards of ethanol for determining the gaseous concentrations.

2.4. *Physico-chemical analysis*

pH of percolate waters was measured by a digital pH meter (Symphony, VWR France, Illkirch, France). A digital differential manometer (vt100 model, Kimo® manufacturer, Canada) was used to determine pressure drop.

3. Results and discussion

3.1. *Acclimatization*

The acclimatization was defined as the required time to achieve high and stable removal efficiency level for a long period (Muñoz et al., 2015). The efficiency profile during this period (121 ± 10 and 124 ± 7 mg carbon m^{-3} air for BF1 and BF2 respectively, Volume Ratio Ethanol/Alkanes (%) 95/5, from 1 to 53 days that is to say period I) was

Table 3
Operating conditions. GAC: Granular Activated Carbon. p: period.

		EBRT (s)	VOCs concentration (mg carbon m^{-3} air)	Volume Ratio Ethanol/Alkanes (%)	Applied inlet load (g VOC m^{-3} package material day^{-1})	Duration (day)
EBRT test	BF1	36	121 ± 10	95/5	290 ± 25	1–53 (pI)
		16	122 ± 5	95/5	660 ± 26	54–75 (pII)
		12	271 ± 24	95/5	1951 ± 173	76–90 (pIII)
	BF2	21	124 ± 7	95/5	519 ± 29	1–53 (pI)
		12	132 ± 8	95/5	947 ± 55	54–75 (pII)
		12	282 ± 23	95/5	2008 ± 163	76–90 (pIII)
GAC test	BF1	12	273 ± 33	95/5	1966 ± 238	91–136 (pIV)
		12	307 ± 50	80/20	2313 ± 402	137–159 (pV)
	BF2	12	279 ± 23	95/5	2008 ± 163	91–136 (pIV)
		12	336 ± 67	80/20	2419 ± 481	137–159 (pV)

equivalent for BF1 and BF2. High functional efficiency was monitored after approximately twenty-five (25) days of functioning: 98.5 ± 1.1% and 99.4 ± 0.9% for BF1 and BF2 respectively. This start-up period has been currently reported by different authors (Aizpuru et al., 2001; Álvarez-Hornos et al., 2011; Cabrol et al., 2012) for removing gaseous mixture of compounds by using biofiltration. Different parameters such as gas characteristics (nature and concentration of chemicals, physico-chemical properties of the chemicals (solubility, saturation vapor pressure, and biodegradability)), operating conditions and packing material characteristics such as changes in moisture content of the packing material, may influence the duration of this step. This delay can also be explained by the development of the microflora within the bioreactor and the selection of the most fitted species to operating conditions. When the biofilter has been inoculated by sludge from full-scale WWTP such as in this study, this delay could be due to changes in terms of growth conditions (attached versus planktonic microflora) and substrate accessibility (food to microorganism ratio) (Cabrol and Malhautier, 2011).

At steady state (21 and 26 days for BF1 and BF2 respectively), removal efficiency remained at very high values: 98.7 ± 0.9% (BF1) and 99.4 ± 0.6% (BF2) for ethanol. The ability to remove alkanes was also high: 82.3 ± 7.0% and 93.2 ± 1.6% for BF1 and BF2 respectively. It should be stressed that the behavior of both biofilters was similar at the end of the acclimatization period.

3.2. *Stratification patterns at steady state*

The longitudinal pattern of biodegradation activity was determined for ethanol and alkanes chemical group at steady state (Fig. 2). The concentration ratio C/C0 against the height ratio h/h200 was represented. C is the concentration of chemicals (mg carbon m^{-3} air) which was measured at the sampled bed height h (m), C0 the concentration of chemicals to be treated (mg carbon m^{-3} air) and the total height of the packing material is called h200 (m).

Fig. 2 A and D revealed that, at steady state, ethanol was almost eliminated (C/C0 = 0.2) on the first 50 cm of the column for BF1 and on the first half of the column for BF2. Alkanes were eliminated on the last 150 and on the second half of the column for BF1 and BF2 respectively when ethanol was almost eliminated.

Stratification in terms of biodegradation with the firstly metabolism of biodegradable compounds and greater penetration of recalcitrant compounds within the filter bed has been reported into previous studies (Aizpuru et al., 2001; Álvarez-Hornos et al., 2011; Cabrol et al., 2012; Bruneel et al., 2018; Flores-Barbosa et al., 2020). This sequential removal may be explained by different assumptions. Short EBRT used in this work probably limit chemical mass transfer of poorly soluble alkanes compounds. Preferential hydrophilic substrate metabolism (ethanol) would be metabolized affecting the metabolism of hydrophobic compounds (alkanes) according to a competition between

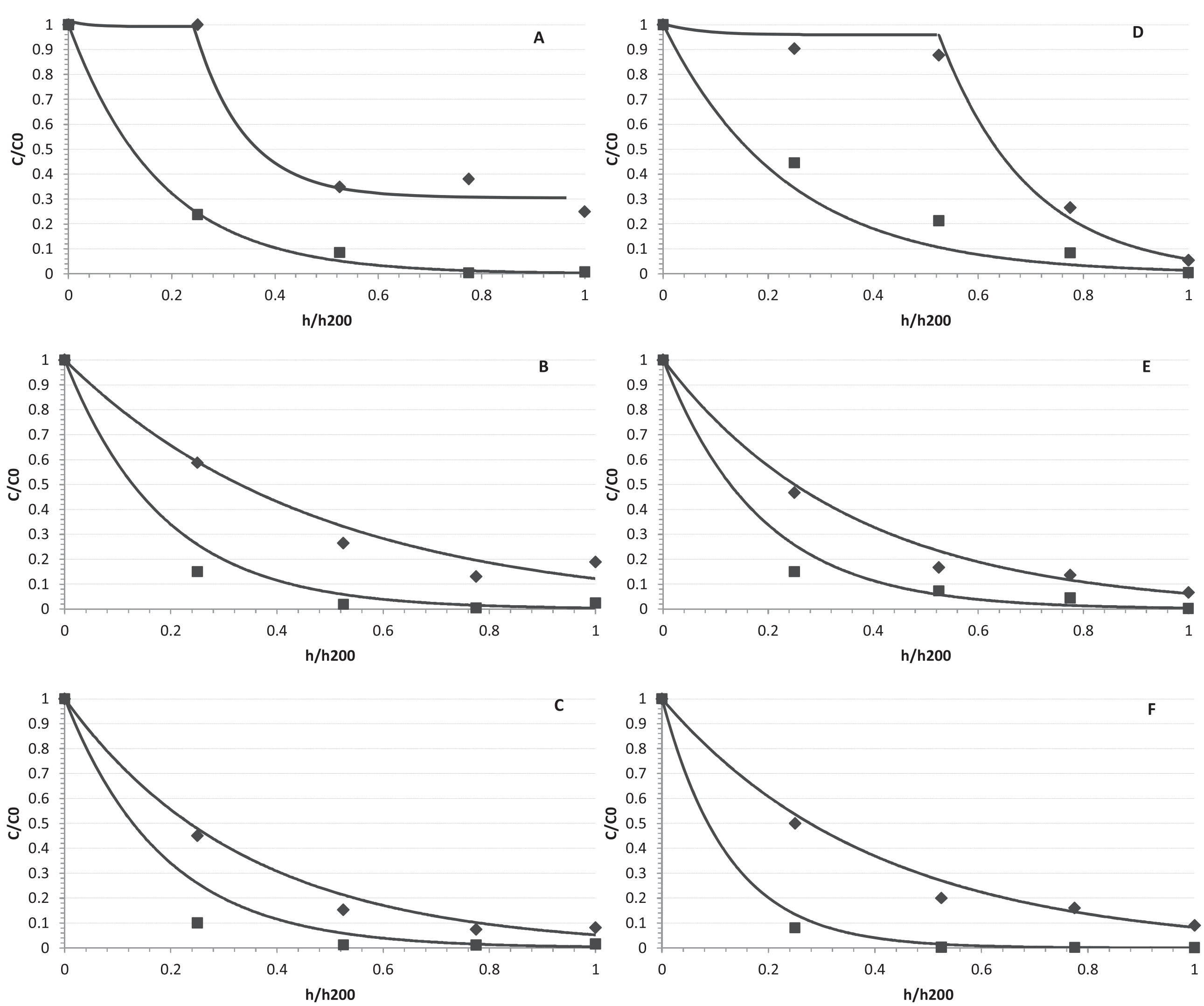

Fig. 2. Temporal dynamics of longitudinal profiles of degradation activities along the bed height at steady state for both biofilters (from 22 to 48 operating days). A, B and C: BF1, EBRT: 36 s; D, E and F: BF2, EBRT: 21 s; A: 22 days; D: 27 days; B and E: 41 days; C and F: 48 days; ■ Ethanol;◆ Alkanes.

substrates phenomenon. The development of different populations along the bed height involved in different compounds removal could explain the obtained result (Cabrol and Malhautier, 2011; Estrada et al., 2013; Flores-Barbosa et al., 2020). These populations could effectively be characterized by different growth rates and/or different substrate and oxygen consumption rates, which results in out competition of populations for oxygen consumption and spatial partition.

Nevertheless, after twenty days of stable running, the dynamic of stratification patterns revealed that the more refractory compounds were removed ($C/C0 \leq 0.1$) on the total height of the column for both BF1 and BF2 (Fig. 2B, C and E, F). Both elimination of ethanol and alkanes within the same compartments could be the result of an arrangement among populations resulting in species coexistence. This phenomenon could be due to functional complementarity through niche complementarity or positive interspecific interactions. These microbe-microbe interactions have been revealed for different microbial communities within natural and engineered ecosystems such as anoxic/aerobic granular sludge in sequencing batch reactors, ammonia conversion in wastewater treatment plants (Junier et al., 2010; Daims et al., 2016; Szabó et al., 2017). It is more probable that a complex network of microbial interactions governs the microbial community activity in this study. These synergetic and competitive interactions within a microbial community were both observed in other engineered ecosystems such as bioreactors used for simultaneously removing nitrogen and phosphorus from wastewaters (Zhang et al., 2017). Concerning VOC elimination, these interactions among co-existing chlorinated ethene, BTEX, and chlorinated methane have been observed by different authors: co-metabolism within aerobic conditions (Leahy et al., 1996; Chauhan et al., 1998; Yeager et al., 2004; Elango et al., 2006; Nagarajan et al., 2015); toxicity of VOC and their degradation products (Hüsken et al., 2001; Furukawa et al., 2005; Justicia-Leon et al., 2012); enzymatic competition (Alvarez and Vogel, 1991; Shim and Wood, 2000; Im and Semrau, 2011); catabolite repression (Aranda-Olmedo et al., 2006; Moreno and Rojo, 2008).

Alkanes concentrations measured along the biofilter bed are plotted versus ethanol concentration (Fig. 3). Similar curves are obtained for both biofilters. After 20 days of operation, removal of alkanes occurred when ethanol RE (Removal Efficiency) values reached 80%. This plotting corroborates a longitudinal biodegradation of ethanol and alkanes. The profiles at $t = 48$ days of operation exhibits the simultaneous removal of alkanes and ethanol. It is probable that ethanol can act as a co-solvent by increasing alkanes partitioning into the biofilm. Mass transfer and bioavailability of alkanes are then favored (Soares et al., 2012). This phenomenon can be also explained by the development of microbial populations degrading alkanes in the section near the gas inlet. Species interactions within microbial communities can be based on metabolic, physical, regulatory and/or signaling parameters. Moreover, these interactions can drive both temporal changes in microbial community composition and function, and spatial organization (Widder et al., 2016). This potential shift of spatial organization could reveal positive metabolic interactions between functional populations. Among several possible mechanisms, it could be assumed that alkanes degrading populations benefits from the metabolite by-products of ethanol degrading populations, such as acetaldehyde and acetate, according to a cross-feeding of excreted metabolites phenomenon (Widder et al., 2016). This exhibits the crucial role of the bacterial community. The imposed operating conditions (applied inlet load (g VOCs m^{-3} filter bed d^{-1}), continuous air stream, microbial seeding, and attached microorganisms-mode development) shaped the biofilter microbiome which impacted the biofilter performance (Cabrol et al., 2016).

3.3. Impact of EBRT

Fig. 4 presents the global elimination capacity versus the applied inlet load. The observed steady state for each tested EBRT clearly highlights that the elimination capacity is quite equal to the applied inlet load. The VOCs mixture elimination is then nearly complete for all the tested applied loads. Both BF maintained a high and stable elimination capacity despite the decrease in EBRT.

Different authors (Cabrol et al., 2012; Álvarez-Hornos et al., 2011; Aizpuru et al., 2003) stressed out the potential of biofiltration to clean industrial waste gases. In this study, such elimination capacity at low EBRT (16 and 12 s) could be explained by the prevalence of hydrophilic and biodegradable compound as both biofilters were fed with a gaseous effluent mainly composed of a biodegradable compound (ethanol/alkanes ratios of 95/5 or 80/20).

Different studies about the treatment of gaseous emissions containing ethanol by using biological processes have been reported by different authors. Some authors evaluated the potential of biological processes to remove ethanol (Hodge et al., 1995; Arulneyam and Swaminathan, 2000; Christen et al., 2002; Pérez et al., 2002; Lim and Park, 2004; Nukunya et al., 2005; Vigueras et al., 2009; Morotti et al., 2011; Lu et al., 2020) or a mixture of chemical compounds containing ethanol (Kiared et al., 1996; Baltzis et al., 1997; Leslous et al., 2004; Jianping et al., 2005; Lim, 2005; Lim et al., 2005; Andres et al., 2006; Sempere et al., 2008; Rizzolo et al., 2012; Soares et al., 2012; Ferdowsi et al., 2017) or ethanol by-product (acetaldehyde) (Duerschner et al., 2020). Different VOCs mixtures, experimental design (filter beds whose volumes were

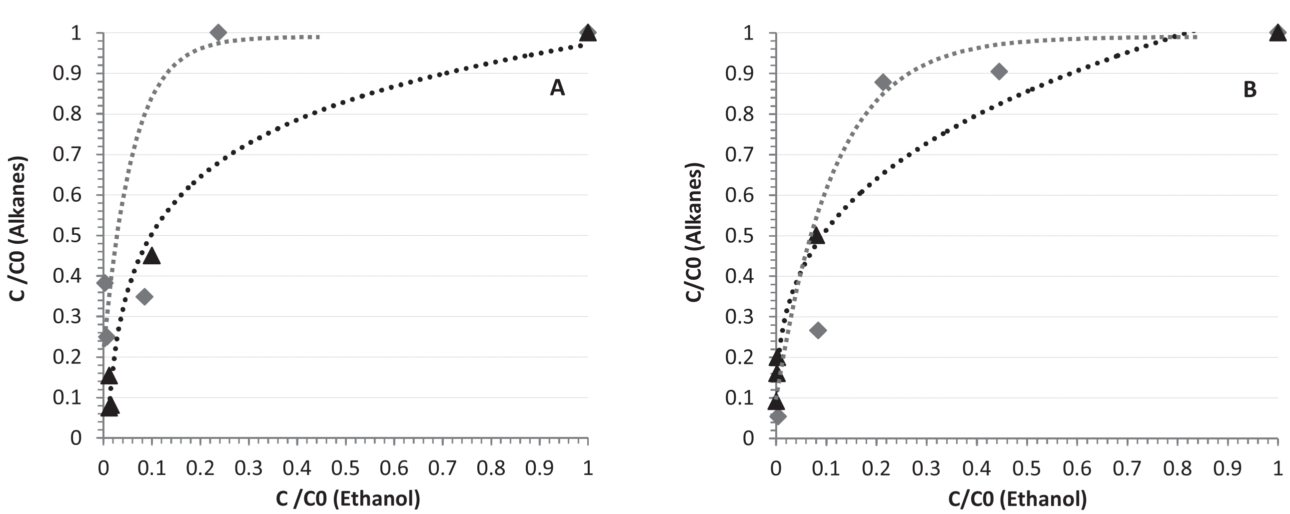

Fig. 3. Alkanes concentration normalized by inlet alkanes concentration versus ethanol concentration normalized by inlet ethanol concentration according to pilot unit of biofiltration, EBRT and sampling day (between brackets). A: ◆ (BF1, 36 s, 22 day), ▲ (BF1, 36 s, 48 day); B: ◆ (BF2, 21 s, 27 day), ▲ (BF2, 21 s, 48 day).

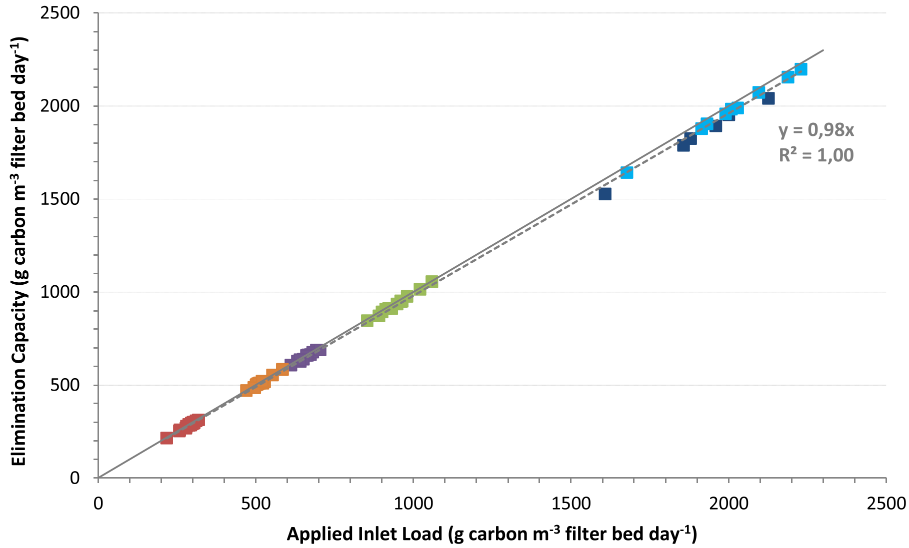

Fig. 4. VOCs elimination capacity for all tested EBRT.

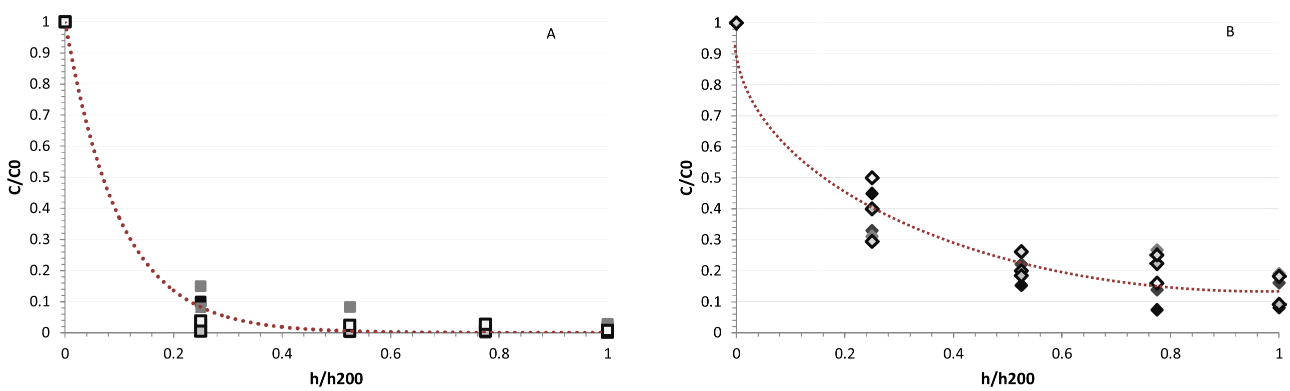

Fig. 5. Longitudinal profiles of degradation activities of ethanol and alkanes at steady state according to pilot unit of biofiltration, EBRT (s), VOCs concentration (mgC m^{-3}) and sampling day. A: Ethanol; ■ BF1, 36, 121, 48; ■ BF1, 16, 122, 69; ■ BF1, 12, 271, 83; ■ BF2, 21, 124, 48; ■ BF2, 12, 132, 69; □ BF2, 12, 282, 83 B: Alkanes; ◆ BF1, 36, 121, 48; ◆ BF1, 16, 122, 69; ◆ BF1, 12, 271, 83; ◆ BF2, 21, 124, 48; ◆ BF2, 12, 132, 69; ◇ BF2, 12, 282, 83.

mainly lower (from 165 mL to 41 L) than the volume used in this study (140 L)), operating conditions (gas velocities mainly lower (from 2 to 3–100 m h^{-1}) than the velocity range (200–600 m h^{-1}) used in this study), packing materials (such as sugar cane bagasse, compost, clay particles) and inocula (generalist inoculum such as compost extract or activated sludge versus specific inoculum such as fungal or bacterial strains) have been considered. Then, it is difficult to exhibit a comparative analysis of all these results although the experimental design carried out in this study seems to be more representative of industrial concerns. Nevertheless, the elimination capacity levels obtained in this work seem to be similar even higher than those observed in previous studies.

Stratification patters (Fig. 5) are similar to those observed at steady-state for an EBRT of 36 and 21 s (Fig. 2C and F). Ethanol and alkanes were mainly removed within the section near the gas inlet, that is to say, 85–100% and 50–70%, respectively, according to the gas velocity and the concentration of compounds. These results seem to confirm positive species interactions between functional populations.

The pressure drop values increased up from 10 to 70 and from 20 to 100 Pa/packing meter for BF1 and BF2 respectively within the study period. Both decrease of EBRT (from 36 to 12 s) and biofilm growth are factors which result in a reduction of the void degree. The pH values of the percolate waters are of 6.2 ± 0,8 and 6.4 ± 0,7 for BF1 and BF2, respectively. These results seem to indicate no buildup of organic acids, mainly acetic.

3.4. Improvement of alkanes biodegradation

In relation to a variable industrial activity, the performance of full-scale biofilters could be influenced by changes of operating conditions in terms of inlet load, residence time of compounds within the biofilter, flow rate. During the assay, the ratio has been modified from 95/5–80/20. These modifications of the gas stream concentration may impact the performance of the biofilter as the part of hydrophobic and recalcitrant compounds increased. Hence, to improve the removal efficiency of hydrophobic compounds and recover similar performance, activated carbon has been tested as packing material in the section near the gas outlet (last 50 cm of filter bed) for BF1. Sawmill wood ships were replaced by a synthetic material without adsorbent properties for BF2. The global concentration of VOCs is indicated on Table 1. The EBRT was 12 s for both biofilters (Table 2, GAC test).

The global performances slightly decreased to stabilize to 93.9 ± 2.2 and 96.7 ± 0.6% (volume ratio of Ethanol/Alkanes of 95/5) and 91.3 ± 2.2 and 94.2 ± 1.3% (volume ratio Ethanol/Alkanes of 80/20) for BF1 and BF2 respectively.

With respect to longitudinal patterns (Fig. 6), ethanol and alkanes are mainly eliminated on the section near the gas inlet: almost 85–90% and 65–70% for ethanol and alkanes respectively and for both BF. As for

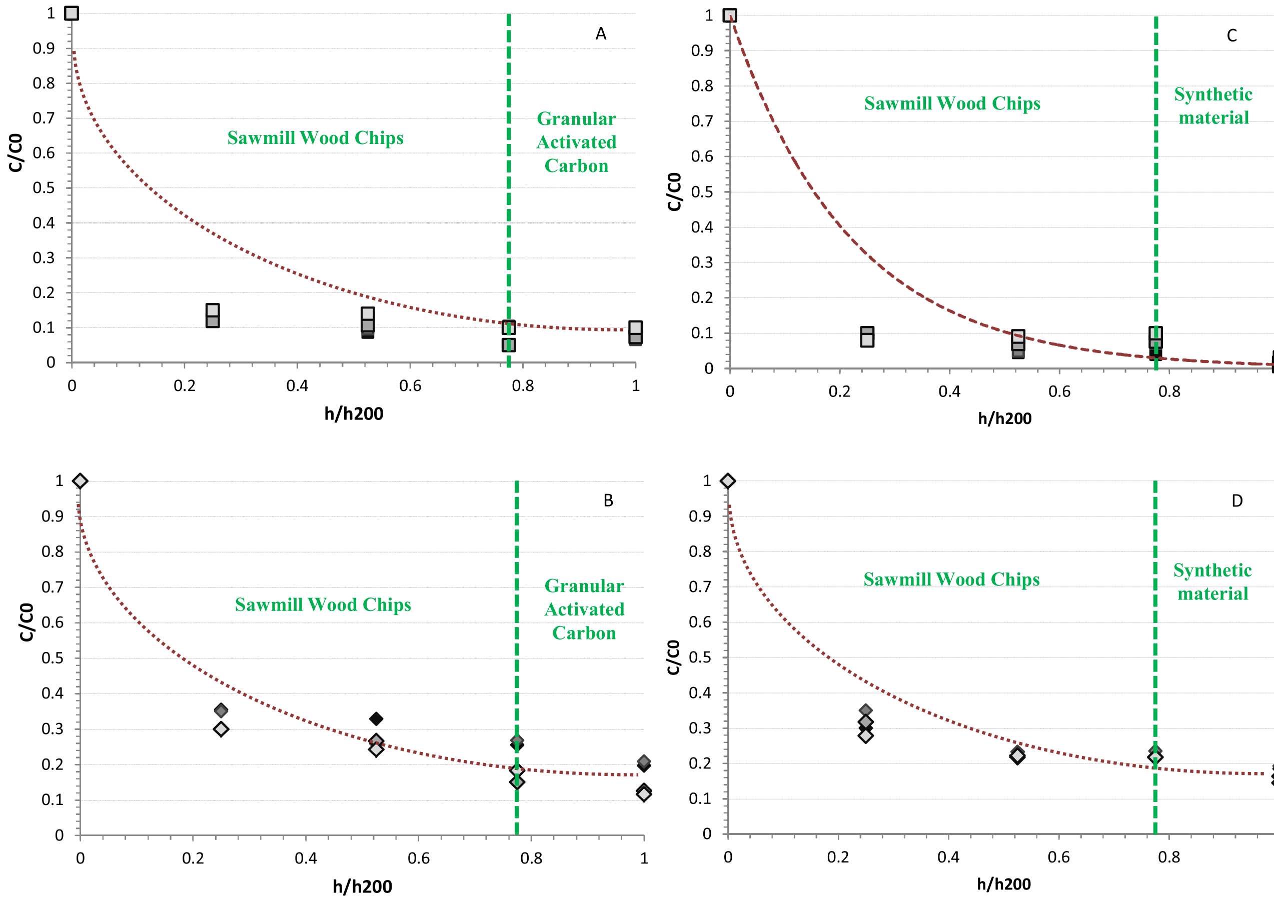

Fig. 6. Spatial patterns of biodegradation activity of ethanol and alkanes according to Ethanol/Alkanes ratio (xx/xx) and sampling day (between brackets) for BF1 packed with sawmill chips and granular activated carbon and BF2 packed with sawmill wood chips and synthetic material. Operating parameters are indicated on Table 2 (GAC test). A: BF1 Ethanol; C: BF2 Ethanol; ■ 95/5 (2); ■ 95/5 (43); ◆ 80/20 (2); □ 80/20 (16); B: BF1 Alkanes; D: BF2 Alkanes; ◆ 95/5 (2); ◆ 95/5 (43); ◆ 80/20 (2); ◇ 80/20 (16).

the last section of both biofilters, it seems that the addition of GAC has no influence on biofilter performances.

This surprising result could be due to the availability of the adsorption sites which is linked to the microbial colonization of the support and the moisture film covering activated carbon particles (hydrophilic properties of activated carbon) and then to the hydrophobic characteristic of alkanes. It has been reported that adsorption phenomena differ in the presence of a biofilm, and in this case, these phenomena seem to work against the adsorption of alkanes on granular activated carbon (Aizpuru et al., 2003; Dorado et al., 2012). Within the upper section of BF1, low concentration of gaseous alkanes even for an Ethanol/Alkanes ratio of 80/20 (around 10 mg carbon m^{-3}) combined with hydrophobic characteristics of alkanes could also explain this result.

4. Conclusion

This work highlights the potential of biofiltration to remove both hydrophilic and hydrophobic compounds within a single pilot unit of biofiltration. Due to the Ethanol/Alkanes ratios (95/5 and 80/20), high performance levels were observed even for low EBRT (16 and 12 s). After twenty days of stable running, the dynamics of stratification patterns can be explained by mechanisms of species coexistence with the setup of persistent trade-offs in the ability of species to exploit available resources (ethanol and alkanes) and to adapt to other operating conditions (moisture content, dissolved oxygen level, local pH value, packing material). These promising results seem to reveal the robustness of these biofilters with the studied operating conditions.

The improvement of alkanes performance by using GAC has not been observed in this study. Nevertheless, as industrial biofilters are usually operated under different ratio Ethanol/Alkanes and compounds concentration, it would be then appropriate to evaluate the system stability of these biofilters in the face of further perturbations, such as transient regimes (recurring shock loads) that are problematic in full-scale applications.

CRediT authorship contribution statement

Claire Moura, Jean-François Després, Jean-Louis Fanlo, Yann Gauthier, Luc Jobert and Luc Malhautier contributed to the formulation of overarching research goals and aims and designed the research. Olivia Gouello, Janick Rocher and Luc Malhautier performed the experiments and collected data. Luc Malhautier wrote the initial draft of the manuscript. Claire Moura, Jean-François Després, Jean-Louis Fanlo, Yann Gauthier, Luc Jobert and Luc Malhautier provided a critical review of the initial draft. The financial support for the project leading to this publication has been provided by Aline Bertin, Jean-François Després and Luc Jobert. All authors read the manuscript and approved it.

Declaration of Competing Interest

There are no conflicts to declare.

Acknowledgments

This work was funded by Manufacture Française des Pneumatiques Michelin through a "Contrat de Coopération dans le Cadre d'Etudes et de Recherches" established in 2018 between Manufacture Française des Pneumatiques Michelin, Olentica sas and IMT Mines Alès.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126614.

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