A COMPARATIVE STUDY OF TWO PROCESSES FOR INDOOR VOCs TREATMENT: BIOFILTRATION VS. HYBRID SYSTEM (BIOLOGICAL PROCESS+ADSORPTION).

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Biofiltration technology and the hybrid system combining biofiltration and adsorption (onto activated carbon) were compared as possible methods to treat indoor air pollution. Toluene and p-xylene at ppb concentration levels (2-45 and 1-33 ppb, respectively) were chosen as characteristic indoor pollutants for this study. An organic material was used as packing material for the biofiltration stage and its acclimation was carried out for 100 days at higher concentrations. Even at low empty bed residence time (EBRTs) and concentrations, toluene removal efficiency reached 100% and p-xylene showed an increasing trend in their removal efficiency over the time. The assessment of by-products and particles generation by the biofilter and the hybrid systems was taken into account. Acetone and acetic acid were identified as by-products of the biofilter. Particle emissions in the range of 0.03 to 10 μm were recorded for both systems which suggest the necessity of using a particle filter at the end of the process chain.

Introduction

The World Health Organization (WHO) recently reported that in 2012, 4.3 million deaths were related to indoor air pollution and 3.6 million were attributable to ambient air pollution (WHO, 2014). In fact, pollution of indoor environments is often much higher than outdoors and is nowadays a public health issue (Geiss et al. 2011). It is estimated that indoor air quality (IAQ) determines, to a large extent, occupant health, comfort and productivity (WCB, 2005). Impacts resulting from poor IAQ include serious health issues (i.e. allergies, asthma, cancers, sick building syndrome, etc.), which give rise to significant costs associated with health care expenses and work performance deterioration (Fisk, 2000; Mendell et al., 2003). In this context, major efforts should be made to enhance IAQ.

Additionally, technological developments have to consider indoor air pollution as a complex subject involving myriad of chemical species (incompletely identified) influenced by environmental conditions which vary in space and time. Furthermore, chemical species are present at low concentrations and have diverse physical-chemical properties. Among these, the volatile organic compounds (VOCs) are major contributors to the deterioration of IAQ. They are emitted by different indoor activities including cooking, burning of candles, open fireplaces, body care, house cleaning, washing, renovation work, the use of electronic devices such as photocopiers or printers, etc. (Salthammer and Bahadir, 2009; Sarigiannis *et al.*, 2011).

Many studies attempt to find an efficient technology to treat these indoor contaminants (Hodgson A.T. *et al.*, 2007; Mo J. *et al.*, 2009; Lu Y. *et al.*, 2010; Lu *et al.*, 2012; Soreanu *et al.*, 2013). Recently, biotechnologies appeared as good alternatives due to their economical and environmental attributes (Lu *et al.*, 2010; Soreanu *et al.*, 2013). Among the biological technologies, biofiltration seems to be the most attractive technique since it has been described as a competitive technology for the VOCs treatment, according to its simple operation, low operating and maintenance costs (Rojo *et al.*, 2012) and its ability to cope with moderately hydrophobic pollutants (Estrada *et al.* 2011). Nevertheless, nowadays, there is no technology capable, alone, of treating indoor air without collateral effects (by-products' generation, high energy consumption, etc.) which leads to the need of coupling different technologies to achieve satisfactory cleaning performance for a sufficiently wide spectrum of pollutants. In this context, the main objective of this research focused on the study of biofiltration and the combination of this technology with adsorption onto activated carbon (hybrid process) to treat indoor VOCs
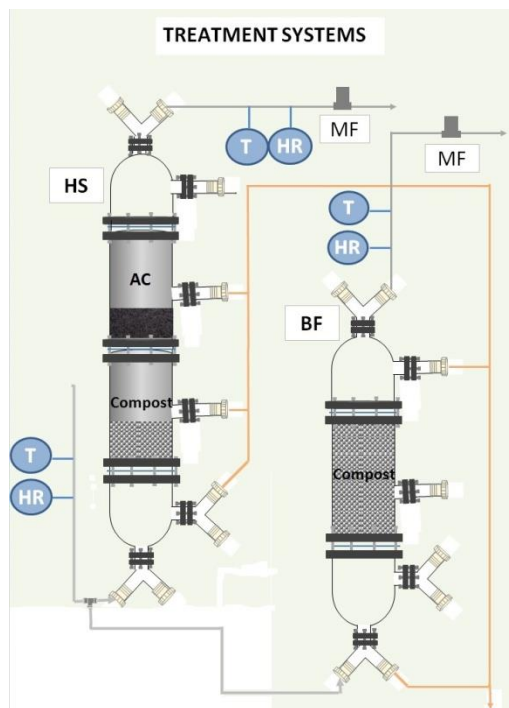
Materials and methods

Figure 1. Experimental setup

The treatment of a mixture of pollutants was carried out in a laboratory scale plant consisting of two reactors operated in parallel (Figure 1) at similar operating conditions (see Table 1). A biofilter (BF) and a hybrid system (HS) (bioreactor + adsorption column) were installed. BF was packed with 3.8 L of a mix of compost and pozzolan at a ratio of 80 %/20 % v/v with a surface area of $5,02\pm0,01$ m^2/g while the filtering media of the hybrid unit consisted of 2 layers (separated between them by a space of about 15cm): the first layer was packed with 1.26 L of the mix of compost and pozzolan and the second layer with 1.26 L of activated carbon (AC).

The AC used in the HS was chemically impregnated for the preferential adsorption of gaseous pollutants such as formaldehyde, ketones and alcohols (C1220 IG 93 Mn from Carbio 12 S.A, France). It is made from coconut, and has a surface area of 867±35m2/g. Two liters of an aerobic activated sludge from a wastewater treatment plant were collected and allowed to decant; then 250 mL of the clarified liquid were taken and added to a nutrient solution and used as inoculum for the compost.

The polluted stream was generated via a permeation device (oven PUL200, from Calibrage) which produces concentrations in the order of a hundred of µg/m^3 (the precision of the concentration standard depends on the compound and is around 5%). To arrive at lower concentrations, closer to what is found in indoor air, a dilution system allows to reach a dilution ratio of 7,35 for the polluted effluent with a maximum flow of 40L/min. The dilution air flow is humidified by passing it through a water bubbler. Relative Humidity (RH) and the temperature were controlled upstream and downstream of the biofilter to monitor the conditions of the biofiltration process (Kimo Instruments and Gefran Coreci, accuracy of 1.5% for RH and 0.3% for temperature measurements). The pre-humidification of the inlet gas stream being not sufficient to provide a good moisture content of the packing material, 90 mL of water was also applied 4 to 5 times a week.

A thermal desorption system (the UNITY 2 from Markes International) was used with the TRACE 1310 Gas Chromatograph (GC) and an ISQ single quadrupole mass spectrometer (MS) (Thermo Fischer Scientific, Inc.) to analyze VOCs concentrations of the inlet and outlet streams. The GC is also coupled to a flame ionization detector (FID).Particles emissions measures were carried out using a real-time particle size spectrometer, the ELPI (Electrical Low Pressure Impactor), which measures airborne particle size distribution in the size range of 0.03−10 µm. An additional study was carried out in order to optimize the Empty Bed Residence Time (EBRT) which is a crucial parameter determining the filter size for a given air flow.

Table 1. Operating conditions.

Reactor	Pollutants	Concentration		Support	EBRT(s) (±1.1%)	Days	T$_{ambient}$ (°C)	RH$_{inlet\ air}$ (%)
		ppb	µg m^{-3}					
BF	Toluene p-Xylene	2-45 1-33	7.6-172 4.4-145	Compost[a]	15-23	155	18-34	34-88
HS	Toluene p-Xylene	2-45 1-33	7.6-172 4.4-145	Compost[a] Luffa AC	2.5-23	155	18-34	34-88
BF EBRT study	Toluene p-Xylene	147 87	556 375	Compost	12 8 6	60	20 ± 2	40± 4

[a]Compost mixed with pozzolan (80%/20%)

The biofilter was designed according to a low EBRT (Empty Bed Retention Time) of 13 s defined as follows:

$$EBRT = \frac{V_b}{Q_v} \quad (1)$$ where Q_v is the volumetric air flow rate (m^{-3} s) and V_b is the filter bed volume (m^3).

The main parameters studied were the inlet load, IL (g m^{-3} h^{-1}), the elimination capacity, EC (g/m^3/hr) and the removal efficiency (RE (%)). EC, RE and IL were determined using the relationships between the toluene inlet concentration, C_{in} (g m^{-3}), the toluene outlet concentration, C_{out} (g m^{-3}), Q_v and V_b:

$$EC = \frac{C_{in} - C_{out}}{V_b} \times Q_v \quad (2)$$ $$RE = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (3)$$ $$IL = \frac{Q_v \times C_{in}}{V_b} = \frac{C_{in}}{EBRT} \quad (4)$$

Results

EBRT study
The air flow was changed in order to get three different EBRTs: 12 s, 8 s and 6 s. The acclimation period for the toluene removal exhibits an exponential trend until RE reaches 100% at day 35 (Figure 2a). After acclimation, the toluene RE (see equation 3) reached 100% for an EBRT of 12 s. A small decrease in RE was registered after EBRT changed to 8 s but 100% RE was recovered and kept it regardless the third change in EBRT. Conversely, the p-xylene removal never exceeded 65% during the entire test, but gradual increases in removal efficiency over the time can be observed on Figure 2b which leads to think that the acclimation period had not finished for this pollutant at the end of the experimental trial. Despite the diminution in RE with every EBRT change, RE increased continuously over the time.
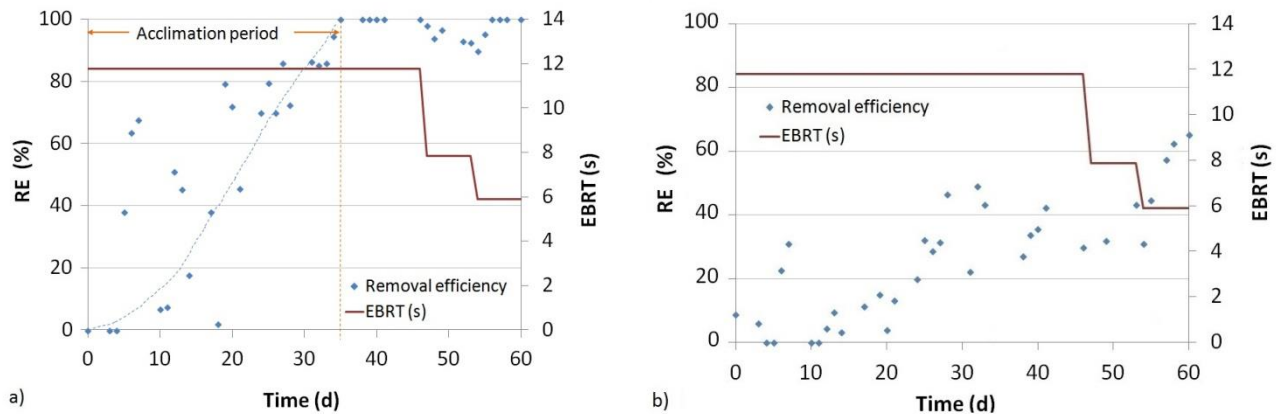

Figure 2. Removal efficiency at different EBRTs for (a) toluene and (b) p-xylene

Overall efficiency of the systems
The influence of the total loading rate (both toluene and p-xylene) on elimination capacity (EC) in both systems is shown in Figure 3. This figure allows comparing in a more reliable way the performance of both systems as EC takes into account both airflow and biofilter size. The red line indicates 100% removal efficiency of the system and this is reached when EC equals the load (Devinny et al., 1999). As seen in Figure 3a, the critical EC for BF was about 22 mg m^{-3} h^{-1}; under this value, mass transfer from gas phase to biofilm was carried out without interferences despite the very low contaminant concentrations in the liquid phase which were calculated based on Henry's law constant and considering the minimum and maximum concentration values for both pollutants in the gas phase. Results are shown in Table 2. These concentrations are indeed low compared to that reported by Roch and Alexander (1997). These authors concluded that a significant mineralization rate and metabolism of toluene could be obtained at a threshold concentration dissolved in water of 0.9 µg L^{-1}, in the presence of other carbon sources and when the medium is inoculated with active bacteria.
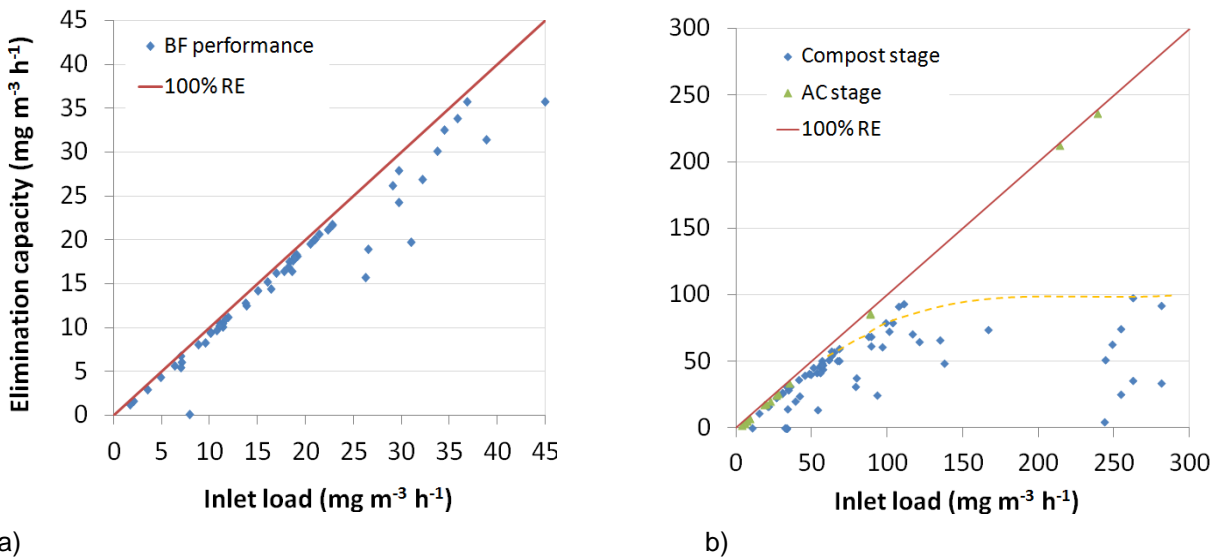
Figure 3. Evolution of the elimination capacity vs. inlet load for (a) BF and (b) HS

Table 2. Calculated contaminants' concentrations in the liquid phase.

Compound	H (24.6°C)	C_g (µg m^{-3})		C_l (µg L^{-1})	
		Min	Max	Min	Max
Toluene	0.258	7.443	167.46	0.289	0.649
p-Xylene	0.300	4.288	141.52	0.149	0.472

C_g: pollutant concentration in the gas phase
C_l: pollutant concentration in the liquid phase

For values higher than 25 mg m^{-3} h^{-1} the amount of toluene diffuse in the biofilm start to be limited as can be seen in Figure 3a and the microbial activity in turn can decrease (Delhoménie *et al.*, 2002). However, maximum EC for this system cannot be defined because higher loading rates were not tested (in accordance with indoor air concentrations). Figure 3b shows a higher EC for compost stage in HS which reached its critical EC near 50 mg m^{-3} h^{-1} and the maximum EC at around 100 mg m^{-3} h^{-1}. At this point, microbial degradation kinetics starts to control biofilter performance (Gallastegui *et al.* 2011). Considering AC stage higher loading rates were eliminated at 100% and neither critical nor maximum EC were reached.

Removal efficiencies in HS by stages
Figure 4 clarifies the role of the two stages (compost and AC) in the HS. As seen, the stage of activated carbon (AC) played an important role when operational conditions changed over the time. For instance, from day 14 to day 29, EBRT changed twice until it reached a value of 2.5 s, which showed the AC stage was more demanded during this period. Specifically, on day 27, 98% of the toluene removal (Figure 4a) and 83% of the p-xylene removal (Figure 4b) was assumed by AC stage. From day 130, concentrations of both compounds significantly increased and in day 140, AC was responsible for more than 80% of the toluene removal and about 75% of the p-xylene removal. Overall results indicate that 18% of the toluene and 51% of the p-xylene loads that entered the HS were treated by the AC stage.

Changes in environmental conditions could also influence the adsorption process. For example, Shin *et al.* (2002) concluded that adsorption capacity of a granular activated carbon for benzene, toluene, and ethylbenzene decreased at relative humidity values over 60% and that this capacity is inversely proportional to the compound concentration. Similarly, Yakout (2014) stated that adsorption increases with the molecular weight of the solute. Other studies had also used the AC together with a biological process (Li *et al.*, 2008; Dorado *et al.*, 2012; Ondarts *et al.*, 2012; Hort *et al.*, 2014; Palau *et al.*, 2015). Dorado *et al.* (2012) used activated carbon as a media of a biofilter. These authors concluded that pollutant adsorption and biodegradation simultaneously took place in the biofilter. They also stated that during the start-up, adsorption phenomenon prevailed over biodegradation.
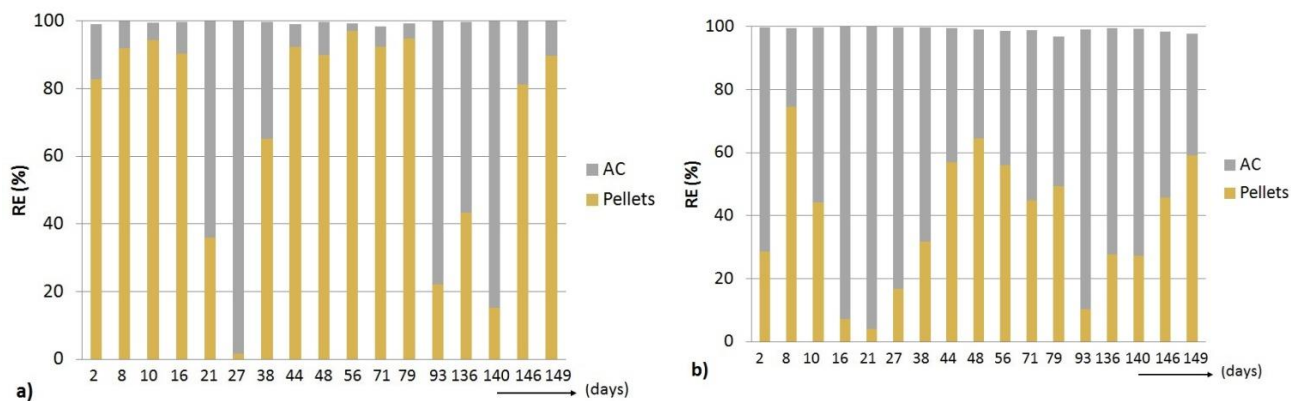
Figure 4. Removal efficiency by stages (compost and AC) in HS during some specific days for (a) toluene and (b) p-xylene

SEM images of the AC at the initial time (day 0) and at day 80 were taken with an environmental scanning electron microscope Electroscan ESEM E3 at 25 kV (accelerating voltage) and magnification of x250 (Figure 5). These photographs show that no microorganisms were present at the starting period whilst some spores were detected at the end coming from compost stage even if these stages were separated by a space of about 15cm. The potential colonization of the activated carbon by microorganism could be considered as a good opportunity as microorganisms could play an important role in the regeneration of the AC bed.
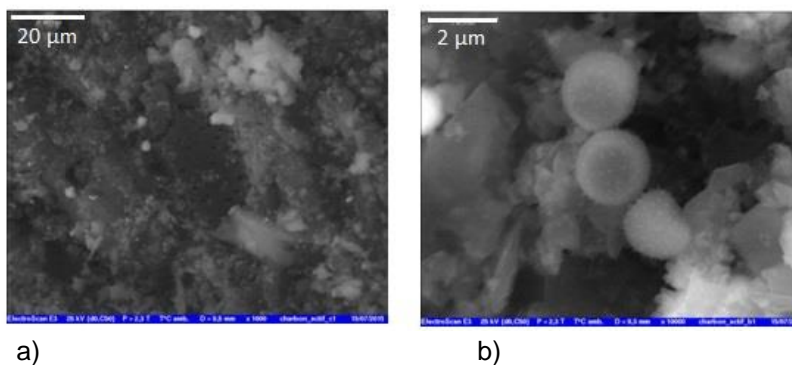

Figure 5. SEM photographs of the AC at a) t=0 and b) t=80 days.

Generation of by-products

Few compounds were identified in the outlet stream of BF and HS by GC/MS analysis. Acetone and acetic acid could be identified in the BF outlet stream. The identification of by-products by HS system was not possible during its outlet stream analysis; only toluene and p-xylene were identified. This might be due to the role of AC stage, because the carbon used in this study was chemically impregnated for the preferential adsorption of pollutants like formaldehyde, ketones and alcohols.

Another explanation for the absence of compounds in the outlet stream of the HS is because some compounds could be retained on the dryer placed before the thermal desorption system during the pre-concentration sample stage in the analytical process which also applies for BF. As a matter of fact, as the dryer is strongly acidic due to the presence of the sulfonic acid groups, in addition to water removal, alcohols and certain other organic compounds which can be converted into alcohols such as aldehydes and ketones would be eliminated (Taurkova *et al.*, 2011). These compounds can be acid catalyzed to react with water and undergo a process called enolization (Carey and Sundberg, 2007) to form an alcohol. Further analyses would therefore be needed in order to determine if another kind of by-products can be generated through these systems.

Emission of particles

There was registered a continuous emission particle from both systems despite the very low air velocity (0.021 m s^{-1}) compared to devices installed in real environments to treat the air (offices, hotels, residences) where the air velocities ranged 2 to 8 m s^{-1}. These velocity values are between 95 and 400 times higher than the air velocity of this study, which means that at real conditions, the emission of particles will be greater.

Consequently, a filter stage after the treatment system would be necessary in order to reduce the number of particles emitted. Nevertheless, a corresponding increase in pressure drop should be considered.

As seen on Figure 6, most of the emitted particles fixed the ultra-fine group in both systems but the HS emitted a higher quantity. Considering the mass of the emitted particles, Figure 7 shows a higher emission of PM_{10} and $PM_{2.5}$ by the HS compared to the BF which could be associated to AC particles (Figure 6 and 7 are presented in the log-Normal distribution, which represent the number or mass of particles per unit volume of air having diameters in the range of log Dp to log (Dp+d(log Dp).
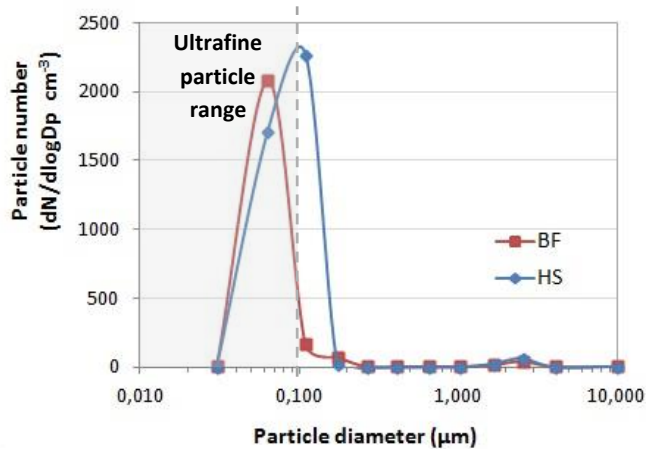

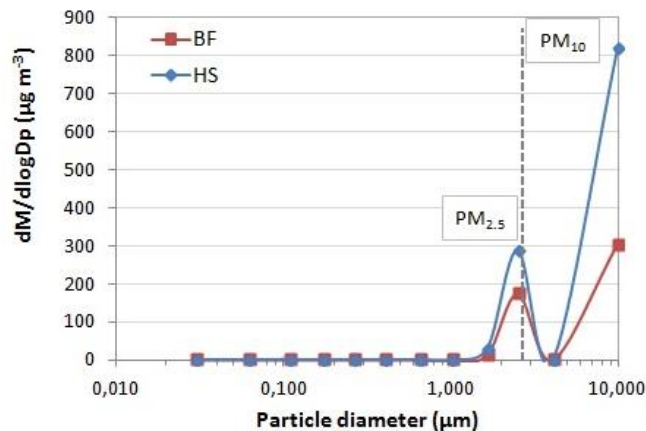Figure 6. Particle size distribution in BF and HS (Dp: particle diameter).

Figure 7. Particle mass distribution in BF and HS (Dp: particle diameter).

Conslusions

It was proved that even at low concentrations biofiltration was able to achieve high removal efficiencies for the target pollutants. Concerning the biodegradation of the target pollutants, toluene was more easily biodegradated than p-xylene by biofiltration, reaching high values of removal efficiency throughout the experimental tests. On the other hand, the acclimation period in the biofiltration process was effectively reduced after the inoculation of the compost with an aerobic activated sludge and the exposure of this to higher pollutant concentrations than those found in indoor environments.

The results highlight the potential of the hybrid system as this showed a higher elimination capacity and was the most robust in front of the heterogeneity of indoor pollutants and operational disruptions. Additionally, the AC stage ensured the treatment of bio-by-products which was only detected in a BF system. It would be fruitful to pursue further research about the optimal ratio of biofiltration and adsorption treatment in order to optimize the hybrid system.

The research raises important questions about the particle emissions of both HS and BF systems in indoor environments. This study measured and quantified only in a narrow range of diameter the emitted particles and in a period of time of one hour. Both HS and BF systems released particles in the range of ultrafine particles, $PM_{2.5}$ and PM_{10}. It would thus be of interest to measure particle emissions in a larger size range and in a larger period of time in order to compare with guidelines (values for 24h). These findings also suggest the necessity of implementing a filter at the end of the treatment process in order to reduce particle emissions but, this new stage in the treatment process could increase the pressure drops. Complementary studies should also be focused on controlling air humidity at the outlet of the systems and quantifying the release of microorganisms.

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