

# Biofiltration of $\alpha$ -pinene vapours using municipal solid waste (MSW) – Pruning residues (P) composts as packing materials

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## A B S T R A C T

In this study, a biofiltration system was designed using mature composts of municipal solid waste (MSW) or MSW mixed with pruning residues (MSW-P) as packing materials to treat vapours of  $\alpha$ -pinene (a dominant volatile organic compounds (VOC) emitted during the MSW-P co-composting). Monitoring the efficiency of the biofiltration system was carried out using a photoionization analyser, a commercial electronic nose (e-nose) and gas chromatography – mass spectrometry (GC/MS). Using an EBRT of 66 s, removal efficiencies for both kinds of biofilters were greater than 90% removal at different stages of the experiment. The acclimatisation periods were 10 and 25 days for the MSW biofilter and MSW-P biofilter, respectively. Removal efficiency of the system was strongly dependent upon the moisture content of the packing materials. As moisture content in the biofilters fell to below 66% for the MSW and 51% (dry basis) for MSW-P, the removal efficiency decreased to less than 90%. E-nose and GC/MS data indicate a complete degradation of the  $\alpha$ -pinene. The e-nose detected a characteristic background emission (odour fingerprint) of each type of biofilter. Results suggest that e-nose's will become a more powerful tool for monitoring VOCs in biofiltration and composting processes in the future.

## 1. Introduction

One of the main problems associated with composting facilities is the odours generated during the process, including the odours produced during the reception and the handling of materials, aerobic treatment and stock piling. The emission of these by-products can cause community annoyance and public opposition to composting plants, not only due to the odours but also due to the potential health risks to workers and inhabitants in the local area [1]. The most important group of chemicals responsible for this odour are VOCs and some inorganic gases (ammonia and hydrogen sulfide) produced during the biodegradation of organic residues [2–5]. The family of terpenes is one of the most representative classes of VOCs emitted during the degradation process of vegetal materials (chips, grass clippings and pruning residues). Amongst them,  $\alpha$ -pinene is frequently the predominant compound, representing between 10.2% and 72.7% of the total emissions [6]. Furthermore,  $\alpha$ -pinene is also emitted by wood processing industries, in particular, saw mills, composite board mills, and paper industries [7,8]. Although, the optimisation of the operational parameters of composting processes is an important objective for

the scientific community in order to reduce the VOCs emissions [5,9]; different techniques exist when the minimisation at source is ineffective. Amongst these techniques, the most widely used are the adsorption on activated carbon, scrubbers and bioscrubbers, condensation, thermal or catalytic incineration, and biofiltration [10–12].

Biofiltration is considered to be an advantageous system for deodorisation due to low operating costs and their ability to treat large volumes of waste gas streams containing low concentrations of odorous compounds [13,14]. Biofilters allow for the conversion of gas-phase chemical compounds to transform into common biological degradation products, such as carbon dioxide, water, and mineral salts. In the bioreactor, contaminated air is passed through a bed of porous and moist medium (packing material), and the contaminants are sorbed to the medium surface where they are degraded by microorganisms [15]. As the treatment of VOCs in this kind of technology requires the transportation of the compound from the gas phase to the biofilm that forms upon a packing material to be available for the degradation by microorganisms [16], the solubility of the compound in water is a limiting factor in the process. For this reason, the study and optimisation of hydrophobic compounds treatment, using biofiltration technology is a challenge for the scientific community [8,17,18].

$\alpha$ -pinene, one of the major hydrophobic compounds, was selected as the marker VOC in this study. Considering the low solubility of  $\alpha$ -pinene in the water phase ( $2.5 \text{ mg l}^{-1}$  at  $23^\circ\text{C}$ ) [19,20], it was interesting to evaluate the treatment of this contaminant through biofiltration technology [21]. Biofilter monitoring is usually carried out using GC/MS and olfactometric techniques when an evaluation of the odours is required [9,22–24].

The use and advantages of e-noses have already been widely reported in order to evaluate the presence of VOCs and odours [25–29]. Nevertheless, few studies have assessed the application of e-noses in the monitoring of biofiltration. Online instruments such as photoionization detector (PID) have also been proposed to obtain rapid information on the concentration of VOCs in different kinds of processes [30–33]. The main advantages of the VOCs analyser are its portability, accuracy, quick response time and reliability in the case of a specific VOC gas (less than 2 s) [28].

This study focused on the evaluation of the VOCs removal efficiency for biofilters that used compost either MSW and MSW-

**Table 1**  
Relevant physico-chemical properties of the packing materials used in the biofiltration system proposed (over dry basis) (average  $\pm$  standard deviation<sup>a</sup>).

		MSW <sup>b</sup>	MSW-P <sup>b</sup>
pH (1:5 extract)		6.55 $\pm$ 0.2	5.60 $\pm$ 0.1
Electrical Conductivity (EC) (1:5 extract)	$\text{mS m}^{-1}$	1245 $\pm$ 0.1	1157 $\pm$ 0.1
Organic Matter	$\text{g kg}^{-1}$	301 $\pm$ 82	842 $\pm$ 93
Kjeldahl-N	$\text{g-N kg}^{-1}$	14.1 $\pm$ 1.4	11 $\pm$ 0.4
C/N		12.6	45.0
Bulk density	$\text{g L}^{-1}$	705 $\pm$ 50	374 $\pm$ 54

<sup>a</sup> Average  $\pm$  standard deviation, over four samples, (d.b.).

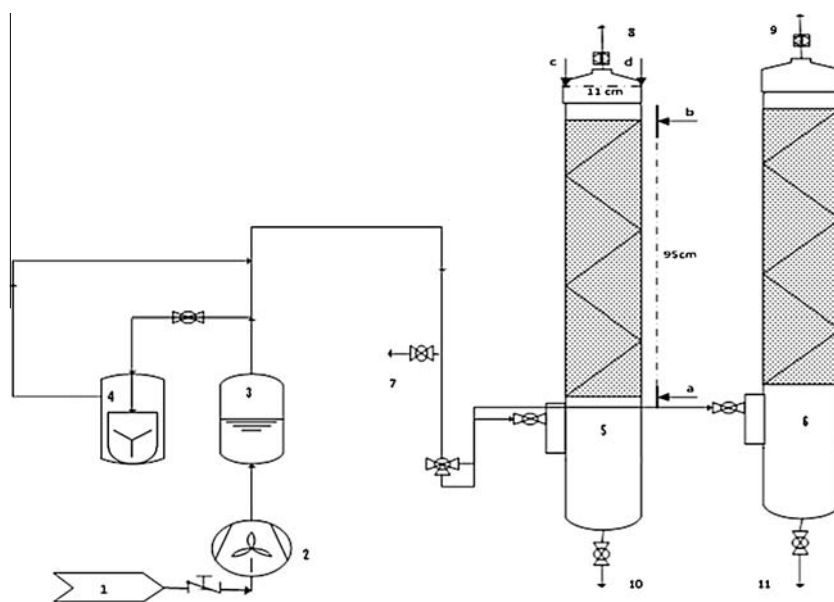
<sup>b</sup> MSW: Municipal solid waste composts; MSW-P: Municipal solid waste – Pruning residues composts.

Pruning residues as the packing material. The biofilters treated an artificial stream of gases containing a hydrophobic VOC ( $\alpha$ -pinene). This evaluation was supported by several analytical techniques, such as VOC analyser, e-nose and GC/MS analysis. There was a particular focus on the removal efficiencies achieved in the biofilters with different moisture contents in their packing materials.

## 2. Materials and methods

### 2.1. Biofiltration unit

The biofiltration system consisted of two laboratory scale biofilters (Fig 1), each using a different type of mature compost as its packing material. Each biofilter consisted of a PVC cylinder of 11 cm in diameter and 1 m in height filled with the packing material in the upper 95 cm (bed volume 9.0 L). One biofilter was filled with compost from MSW and the other one with a mixture of compost from MSW and Pruning residues (*P*) in a volumetric ratio 1:1. Some relevant physico-chemical characteristics of the packing materials are shown in Table 1, additional details can be found in Delgado-Rodríguez et al. [5]. The granulometry of both packing materials was from 7 to 20 mm, in order to improve removal efficiency and avoid operational problems (clogging and control of air flux). The packing materials had previously been used to treat a gas stream composed of a VOC mixture from the active composting of



**Fig. 1.** Schematic diagram of the biofiltration system. (1) Ambience air; (2) Compressor; (3) Humidifier; (4)  $\alpha$ -pinene sparger; (5) Biofilter compost MSW; (6) Biofilter compost MSW-P; (7) input sampling port; (8 and 9) outlet biofilter gas/output sampling port; (10 and 11) Water drainage.

MSW for up to two months [28]. Due to this fact and that natural materials were used as bed packing, no inoculation was performed. The initial moisture content of the packing materials was determined by oven drying at 105 °C. During the course of the experiment the moisture content of the packing materials was controlled periodically by measuring the difference in weight between the complete biofilter bed and its initial weight. When the addition of water was necessary, it was added to the top part of the biofilter. As the nature of the materials was different, the moisture content was expressed as a percentage of the sample's dry weight (d.b.) to be able to compare each medium.

The inlet gas stream was supplied from the bottom of the column (ascending flow). Oil-free compressed air was humidified to 90–100% by sparging. In order to generate the contaminated airflow, a small fraction of humidified air was fed to a sparger, which contained liquid  $\alpha$ -pinene (Merck, >95% purity). Subsequently, this stream was joined to the main distribution line and introduced into the biofiltration system. The inlet concentration of the contaminant was adjusted by the flow rate of the gas stream with  $\alpha$ -pinene; guaranteeing the concentration of the contaminant fixed during 6–8 h. The average  $\alpha$ -pinene concentration during all the stages of the experiment was 11.6 ppm<sub>v</sub>. The empty bed residence time (EBRT) was adjusted to 66 s. EBRT values of about a 1 min are frequent in biofiltration experiments in order to obtain effective degradation in the system [28,34–37].

The experiment was separated into four stages, modifying some operative conditions of the system proposed: (i) Days 1–40 –  $\alpha$ -pinene concentrations below 5 ppm<sub>v</sub> with maximum moisture content of the packing materials; (ii) Days 80–144 – Gradual increase of the  $\alpha$ -pinene concentration in the inlet gas stream of up to 1600 ppm<sub>v</sub>, (iii) Days 154–184 – Decrease of the packing material moisture content with a constant  $\alpha$ -pinene concentration in the inlet gas stream of 1600 ppm<sub>v</sub> and (iv) Days 185–266 – Increase of the packing material moisture content with a constant  $\alpha$ -pinene concentration in the inlet gas stream of 1600 ppm<sub>v</sub>.

## 2.2. VOCs analyser measurements

Rapid *in situ* measurements of the  $\alpha$ -pinene concentrations were performed in the sampling ports using a portable VOCs analyser fitted with a 10.6 eV lamp for photoionization (MULTIRAE IR, PGM-54, RAE systems, San José, CA, USA). The sampling ports were located immediately before the inlet stream of contaminated air and at the output of each biofilter (1). The instrument sensitivity was 0.1 ppm<sub>v</sub> in a concentration range from 0 ppm<sub>v</sub> to 200 ppm<sub>v</sub>. The suitability of this instrument for semi-quantitative measurements of VOCs has been reported in a number of studies [5,30,38]. As  $\alpha$ -pinene is the only VOC in the inlet gas stream, the response of the PID detector is directly proportional to its concentration. The instrument was calibrated with isobutylene, as recommended by the manufacturer, and therefore all the readings obtained were transformed to  $\alpha$ -pinene concentrations using a correction factor of 0.31 [39].

Gas samples were taken from the inlet and outlet sampling ports of both biofilters (MSW and MSW-P) by means of an internal sampling pump with a flow rate of 0.150 L min<sup>-1</sup>. The readings were registered during each sampling when signal stabilisation was observed, usually in a time less than 30 s. Replicate measurements were taken three times in each sampling port on a daily basis.

This instrument does not detect water, but condensation on its UV lamp could produce biased readings [38]. For this reason, a teflon filter (0.2  $\mu$ m pore size) was used as a water and particulate material trap. The removal efficiency was determined as present in the following equation:

$$RE = \frac{(C_{in} - C_{out}) \times 100}{C_{in}} \quad (1)$$

where RE: removal efficiency (%); C<sub>in</sub>: Inlet  $\alpha$ -pinene concentration (ppm); C<sub>out</sub>: Outlet  $\alpha$ -pinene concentration (ppm).

## 2.3. Electronic nose analysis

The e-nose is a commercial combination of chemical sensors and software for the recognition of the pattern signs or odour fingerprint of the gaseous samples. A PEN3 e-nose (Portable Electronic Nose, Airsense Analytics GmbH, Hagenover, Schwerin, Germany) was used to analyse the gases before and after the biofilters (at the sampling ports), similar to the measurements with the VOCs analyser. The e-nose consists of an array of 10 different metal oxide sensors (MOS) positioned inside a flow chamber (1.8 mL). The analytical system has an integrated sampling system, which by automatic control (autoranging) prevents overloading of the sensors, and also leads to a better and faster qualitative and quantitative analysis. Sample measurements were taken in replicates with ambient air being used as a blank for the experiment. The signal stabilisation took approximately 60 s for the total range of  $\alpha$ -pinene concentrations, however the data used for the statistical analysis corresponded to the final 10 s of the sampling time. Also, a time of 60 s was used as a purging time between consecutive measurements. Principal component analysis (PCA) was used during the data collected and reduction for samples taken between days 88 and 223 of the experiment. This procedure uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components. The data reduction is displayed in two-dimensional plots, in which the axes correspond to the first two principal components and samples are distributed in this two-dimensional space. The legends for the x- and y-axes contain the value of the variance achieved by the PCA component. This statistical analysis was carried out by the e-nosés built-in software [40].

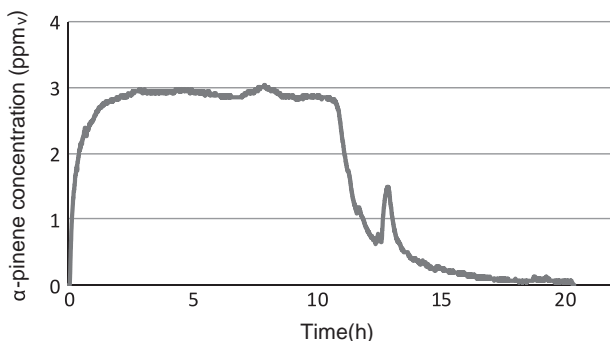
## 2.4. GC/MS analysis

The sampling for the chromatographic analysis was performed during day 0 and day 184 of the experiment. The samples were taken from both sampling ports of the MSW and MSW-P biofilter, using tedlar bags with a capacity of 3 L. Samples were stored at room temperature in darkness for 24 h before each analysis.

From each sample, an aliquot of 0.5 mL gas was injected with a gas syringe, whereas the rest of the sample was pre-concentrated

**Table 2**  
Instrumental parameters used in the determination of VOCs by GC/MS.

Type	Shimadzu GCMS-QP2010SE		
Injecting port	Split less		
Injector temperature	250 °C		
Detector temperature	230 °C		
Capillary column	HP-5MS (Agilent)		
	30 m × 0.25 mm i.d. × 0.25 $\mu$ m		
Column linear velocity	36 cm/s (1 mL/min)		
<i>Oven program</i>			
Initial temperature	35 °C		
Initial time	5 min		
	rate (°C/min)	Final temp (°C)	Final time (min)
	5	270	20
<i>Mass spectrometer</i>			
El voltage	70 eV		
Mass range, scan mode	m/z 30–550 amu		
Solvent delay	0 min		



**Fig. 2.** Evolution of  $\alpha$ -pinene concentration in the inlet stream during the acclimatisation phase of biofilters.

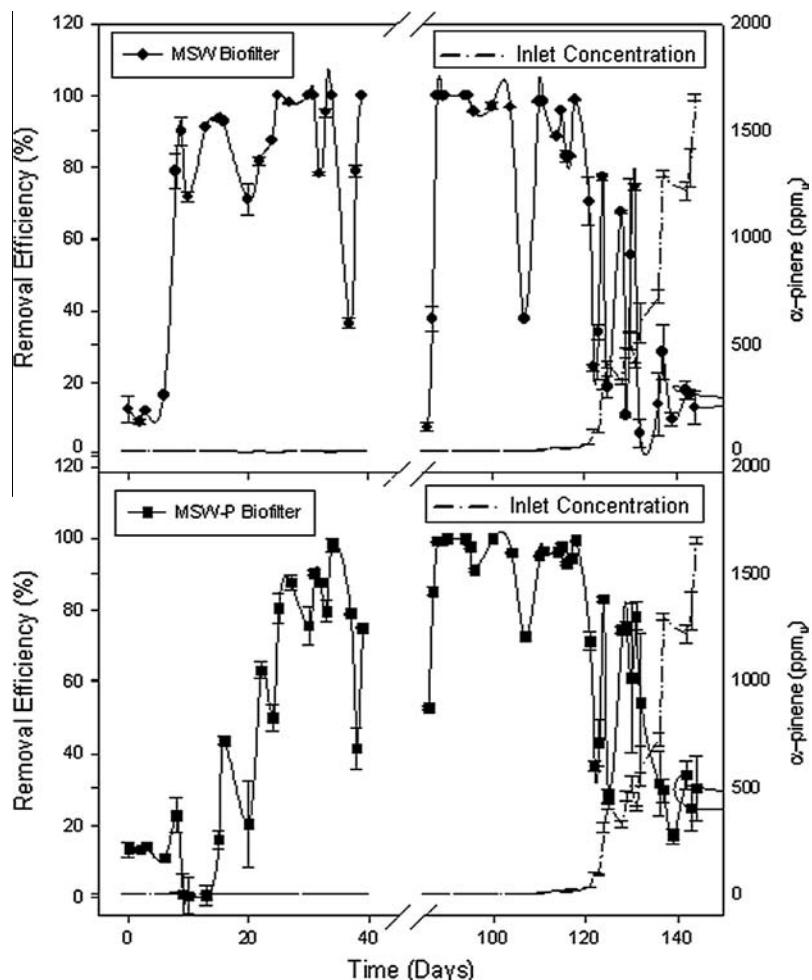
prior to its analysis using the solid phase microextraction method. A SPME fibre coated with 75  $\mu\text{m}$  carboxenopolydimethylsiloxane (Supelco, Bellefonte, PA, USA) was used to capture VOCs in the tedar bag. The SPME fibre was inserted into the bag for 30 min. The SPME coating fibre containing the VOCs, was inserted into the GC injection port at 230  $^{\circ}\text{C}$  and maintained for 3 min for desorption. After each sample injection, fibres were inside the SPME needle to prevent possible contamination and were conditioned before re-use with helium at 250  $^{\circ}\text{C}$  for 10 min. The desorbed volatile compounds were performed using a gas chromatograph- mass

spectrometric (GC-MS) Shimadzu GCMS-QP2010SE (Shimadzu corporation, Kyoto, Japan) using the conditions described in Table 2.

### 3. Results and discussion

The  $\alpha$ -pinene concentration in the inlet gas stream was maintained during a period of 5–10 h each day, depending on the stage of the experiment. Fig. 2 shows the tendency of the VOCs detector signal observed during the complete experiment. The highest concentration reached was 3 ppm<sub>v</sub>, which corresponds to the acclimatisation phase of the biofiltration system. All measurements were performed when the signal of the VOC's detector was constant, as shown in 2, so that results could be compared.

Fig. 3 represents the  $\alpha$ -pinene removal efficiency of the biofilters during the first 140 days. In the first stage of the experiment (1–40 days), the moisture of the packing material was maintained within a range of 112–101% (d.b.) and 100–89% (d.b.) for MSW and MSW-P biofilter, respectively. During this period, the acclimatisation of the system occurred; MSW biofilter needed approximately 10 days to reach  $\alpha$ -pinene removal efficiency greater than 90% whereas MSW-P biofilter removal efficiency reached 80% after 25 days. Previous studies reported that short acclimation periods were found in biofiltration systems when the materials used as beds (compost and wood chips) had been aged for six months, allowing the production of terpenes and the appearance of microorganisms adapted to this carbon source [20]. On the other hand,



**Fig. 3.** Removal efficiency (%) and inlet concentration (ppm<sub>v</sub>) of  $\alpha$ -pinene in the biofiltration system (0–140 days).

Jin et al. [41] reported acclimation periods of 28 days before complete removal of  $\alpha$ -pinene took place whereas Van Groenestijn and Liu [7] found acclimation periods from 4 to 8 weeks.

In this case, It is important to have in mind that despite the packing materials had also been used before to treat exhaust gases coming from kitchen waste and pruning residues composting [28], which suggests that the microbial community present in the packing material had adapted to the  $\alpha$ -pinene, the start-up periods obtained were between 10 and 25 days which are in the range of the normal periods reported when natural packing materials are used, but were not reduced by the aged of the compost used as bed in previous experiments, possibly due to the inactivation of the microbial community as a consequence of the moisture reduction, occurred in the packing materials between the experiments. In the 2nd experimental stage (days 80-144), the  $\alpha$ -pinene concentration in the inlet gas stream was progressively increased to a maximum of 1800 ppm<sub>v</sub>. The removal efficiency of the biofilters decreased to below 90% as  $\alpha$ -pinene concentrations was increased over 30 ppm<sub>v</sub>. Fig. 3 shows a significant decrease in the removal efficiency as soon as the  $\alpha$ -pinene concentration in the inlet gas stream increased. The same effect was observed immediately after several non-operational days of the system. An example of this is the abrupt decrease of the removal efficiency observed in day 107, immediately after a non-operational period. These temporary efficiency reductions would indicate that the biofilters needed a re-acclimation time [42].

After a sharp decline of the efficiency in the system occurred on day 121 (Fig. 3), which corresponded to the higher inlet concentrations, improved performance was observed for the treatment of  $\alpha$ -pinene by MSW-P biofilter. Specifically, when the concentration of the compound in the inlet gas stream was 672 ppm<sub>v</sub>, the average efficiency was 33.8% and 48.4% in MSW and MSW-P biofilter, respectively. These figures corresponded to an elimination capacity

of  $\alpha$ -pinene by the system of 79 g m<sup>-3</sup> h<sup>-1</sup> (MSW biofilter) and 113 g m<sup>-3</sup> h<sup>-1</sup> (MSW-P biofilter). Mohseni and Allen [8] and Mohseni et al. [43] reported lower elimination capacities (40–45 and 30–35 g m<sup>-3</sup> h<sup>-1</sup>) for  $\alpha$ -pinene using similar packing materials, with EBRTs of 20 and 45 s, and inlet concentrations of 109 ppm<sub>v</sub> and 40 ppm<sub>v</sub>, respectively. Similarly, Bagherpour et al. [20] reached values for this efficiency parameter of 211 g m<sup>-3</sup> h<sup>-1</sup> with an inlet  $\alpha$ -pinene concentration of 114 ppm<sub>v</sub>. However, no previous studies have reported inlet  $\alpha$ -pinene concentration that are greater than or equal to the maximum used in this study, suggesting that the proposed biofiltration system would expand the range of working concentrations.

In the third phase of the experiment, from day 154 to day 184 (Fig. 4), the moisture content of the packing materials was reduced progressively by eliminating the humidification unit. The inlet  $\alpha$ -pinene concentration was also set at 17 ppm<sub>v</sub>, based on the results obtained from the previous stages, where removal efficiency was highest (at this concentration). The study aimed to observe the influence of the moisture content on the performance of the two biofilter systems after a transition phase of 3 days was used for acclimatisation. After this period, when the moisture content was 77% (d.b.) and 91% (d.b.) for the MSW and MSW-P biofilter, respectively, the removal efficiency for both biofilters was 100% (Fig. 4). The biofilter performance however was adversely affected when the moisture content of the packing materials was set below 66% for MSW biofilter and 51% for MSW-P biofilter with removal efficiencies observed to be lower than 90%. As is shown in Fig. 4, despite the hydrophobic nature of the contaminant, there is a direct relationship between the removal efficiency and the moisture content of the packing materials. These results indicated that the optimum moisture content range for the packing materials and the EBRT used in this experiment was between 66% and 112% (d.b.) in the case of the MSW biofilter and between 51% and 100% (d.b.)

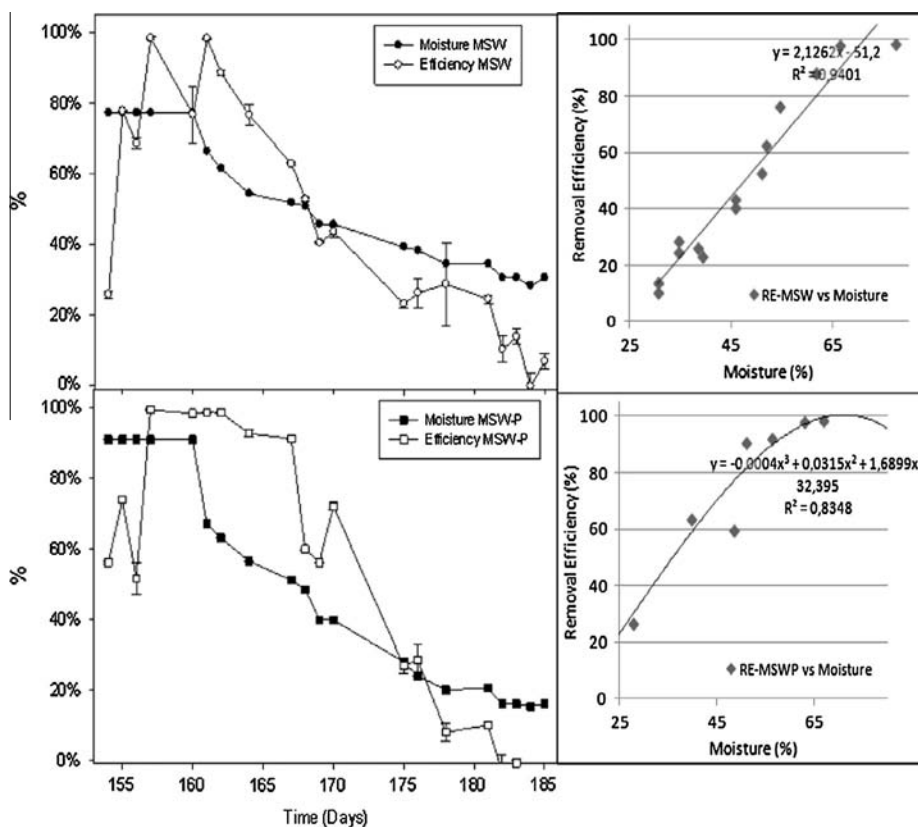


Fig. 4. Biofilters performance during the decrease of the moisture content of the packing materials.

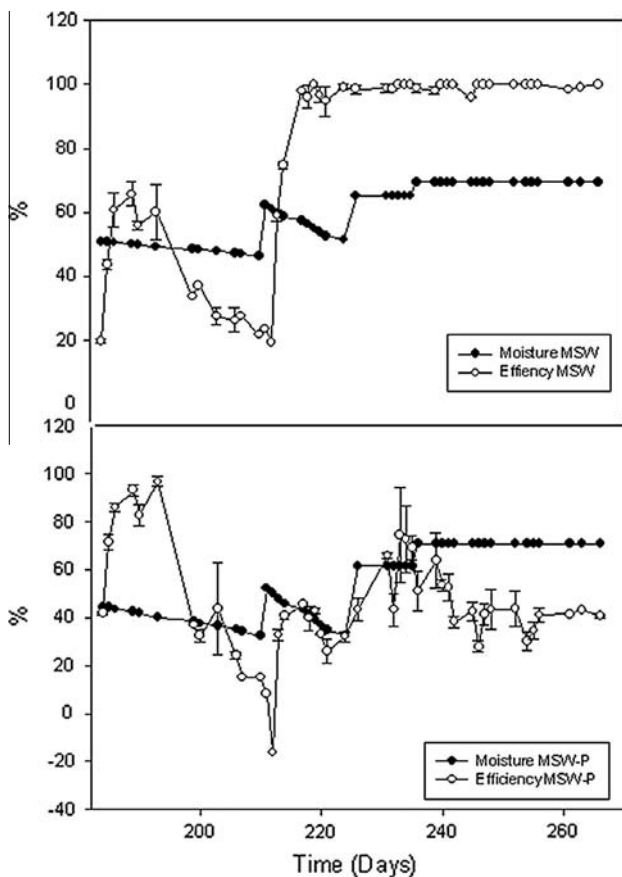


Fig. 5. Assessment of the biofilters adaptation capacity during the replacement stage of the beds moisture content.

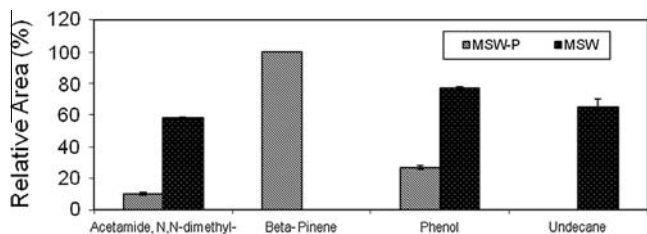


Fig. 6. Main volatile organic compounds found in the biofilters by GC/MS on day 0.

for MSW-P biofilter, respectively. These results are consistent with those found in previous studies [44], where the minimum moisture content suggested for the packing material was reported as 66% (d.b.).

The four study stage was carried out between day 185 and day 266 (Fig. 5). In this stage, the moisture content was increased progressively up to the optimal reported values in order to evaluate the adaptation capacity of the packing materials. The average inlet concentration of  $\alpha$ -pinene during this stage was 11.6 ppm<sub>v</sub>. Although the moisture content of both packing materials was adjusted progressively to the optimum range found in the previous stage; only MSW biofilter was able to reach a removal efficiency of 100%, whereas MSW-P biofilter removal efficiency stagnated at a value around 40%. It is noticeable that the 100% of removal efficiency in MSW biofilter was achieved after 34 days from the start of the stage, once the moisture content had been adjusted to the lower limit of the optimal range.

Fig. 6 shows the results of the GC/MS data obtained during sampling performed on day 0. In this figure, the different peaks observed for each compound were integrated and normalised considering 100%, the highest possible signal. These results show that even though the VOC detector signal was 0 ppm during sampling, the biofilters had different background emission that are dependent on their packing material characteristics. Another factor might be a consequence of their previous use of the packing materials in previous biofilter [28]. Although almost all VOCs found in this sampling were previously reported as common emissions in composting processes [9], the beta-pinene emission findings may indicate a natural fingerprint by the components of the packing material used, as this peak corresponds to the biofilter with a vegetal origin. It is also possible that the terpene based compounds could have come from the ambient air. No compound related with anaerobic conditions was found, despite the high moisture content at the beginning of the experiment. In addition, it is possible that the acetamide, N, N-dimethyl peak may be an artefact caused by the solid phase microextraction method, as this compound is a solvent commonly used for fibres.

To avoid this interference, the next analysis was carried out by injecting 0.5 ml of the gas directly into the GC/MS. The chromatograms in Fig. 7 show the analysis of the gas samples taken from all the sampling ports during day 266 of the experiment. The associated concentrations of  $\alpha$ -pinene determined by the VOC detector from all samples were 17.6 ppm<sub>v</sub> in the inlet stream, 0.0 ppm<sub>v</sub> in the MSW biofilter output and 10.4 ppm<sub>v</sub> in MSW-P biofilter output, respectively. These results clearly indicate that the main and more representative compound was  $\alpha$ -pinene. However, there were other VOCs present in the chromatograms, which could be impurities of the reactive or natural compounds present in the surrounding air. These compounds were octadecanoic acid, the 1, 2-cyclohexanediol, other organic acids and terpenes (limonene, camphene, careen and beta-pinene). Similar to the sampling of day 0, undecane and phenol were present with maximum peaks in samples corresponding to MSW biofilter, while beta-pinene seemed to be only prominent in MSW-P biofilter. However, these compounds were also present in the input stream, which suggests that they were present in the ambient air and entered into the biofilter systems.

The high removal efficiency reported by the VOCs detector was consistent with the results from the GC/MS analysis. The  $\alpha$ -pinene signal in the chromatograms (Fig. 7) disappears completely if it is compared to the input stream and the MSW biofilter samples. Table 3 shows the concentration of the VOCs found on day 266 in the sampling ports using GC/MS. In the same way as in the chromatograms, most compounds found in the GC/MS analysis are absent in MSW biofilter samples. Moreover, the average efficiency of MSW-P biofilter at this moment of the experiment is represented in these results. GC/MS analysis did not detect compounds related to a partial degradation of the  $\alpha$ -pinene in the biofiltration system.

Fig. 8 presents the PCA carried out using the response of 5 metal oxide sensors and the dilution factor of the e-nose used in the experiment on day 88 of the experiment. This statistical analysis was performed when the output concentration of  $\alpha$ -pinene in the biofilters was the same, aiming at detecting any possible influence of the packing material on the results. In this case, the removal efficiency was determined to be 100% in MSW biofilter and 99.2% in MSW-P biofilter. All the PCAs performed showed good discrimination power values for the input classes chosen. The discrimination power is a measure of the overlapping of two groups of measurement points. The less they overlap, the better they can be distinguished. On this particular day the associated variance of the two principal components in PCA was 99.94%, which means that the system was represented correctly by these two new uncorrelated variables. MSW and MSW-P biofilter groups were mainly separated

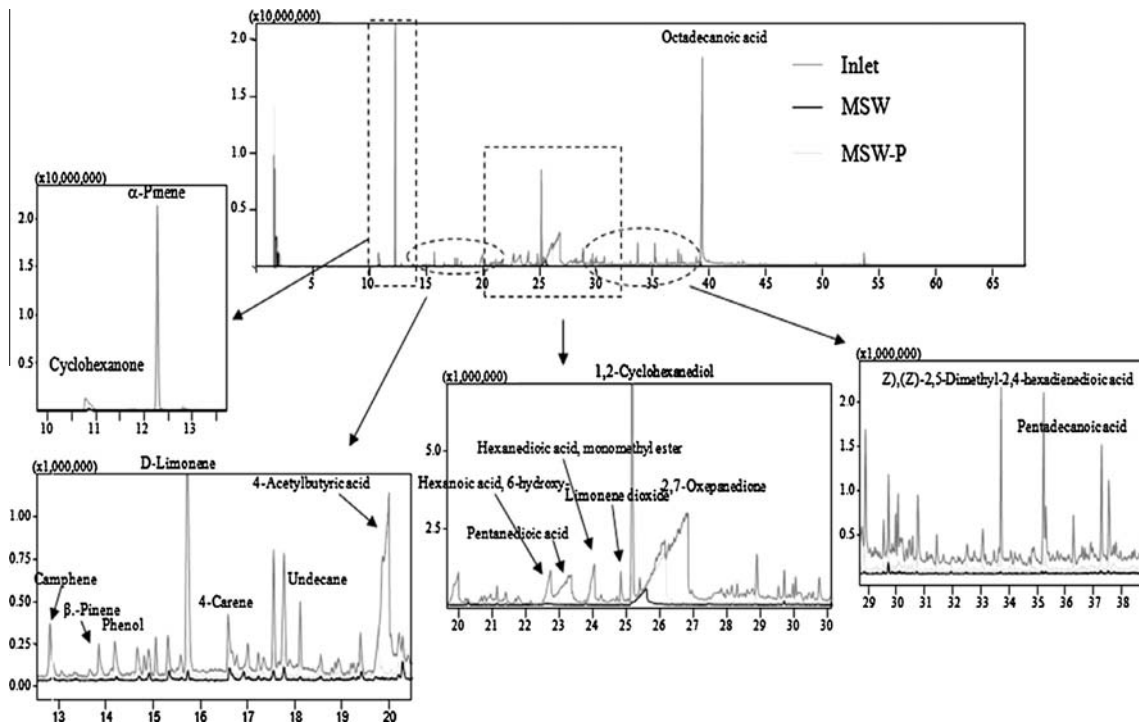


Fig. 7. Chromatograms obtained by GC/MS of gas samples from the inlet stream and output samples from the biofilters on day 266.

**Table 3**

Concentration of the main volatile organic compounds found on day 266 in the different sampling ports using GC/MS (average  $\pm$  standard deviation<sup>a</sup>).

		Inlet	MSW <sup>b</sup>	MSW-P <sup>b</sup>
$\alpha$ -Pinene	$\mu\text{g L}_{\text{air}}^{-1}$	1969 $\pm$ 184	n.d.	1205 $\pm$ 114
$\beta$ -Pinene	$\mu\text{g L}_{\text{air}}^{-1}$	16 $\pm$ 1	n.d.	20.8 $\pm$ 0.51
3-Carene	$\mu\text{g L}_{\text{air}}^{-1}$	16.0 $\pm$ 0.5	n.d.	3.04 $\pm$ 0.18
D-Limonene	$\mu\text{g L}_{\text{air}}^{-1}$	103 $\pm$ 3	n.d.	13.7 $\pm$ 2.1
Undecane	$\mu\text{g L}_{\text{air}}^{-1}$	13.5 $\pm$ 1.8	n.d.	n.d.

n.d.: Not detected.

<sup>a</sup> Average  $\pm$  standard deviation, over four samples.

<sup>b</sup> MSW: Municipal solid waste composts; MSW-P: Municipal solid waste - Pruning residues composts.

along the  $\chi$  axis (Function 1), which accounted for 97.88% of the total variance. In all cases, the variance of the axis, which represents the function where the separation occurred, accounted for variances over 70%. The results indicate that the e-nose detected a fingerprint that allowed differentiation between the outputs signals of the packing materials used in the biofiltration systems. The loading analyses carried out, showed that the differentiation of classes is caused by the signal of the broad-range (W5S) and the aromatic-aliphatic (W5C) sensors. The W5C sensor is reported to be sensitive towards alkanes, aromatic compounds and less polar compounds. Previous studies [28,45] reported similar results using different composts as packing materials and composting processes.

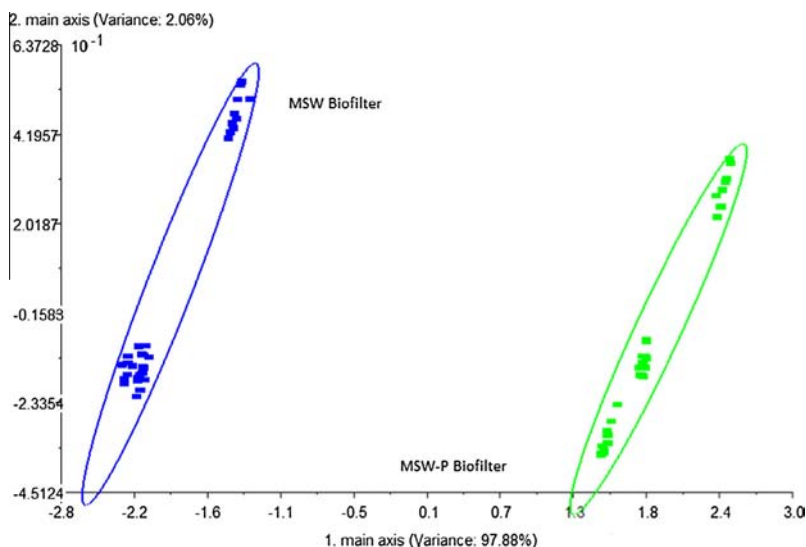
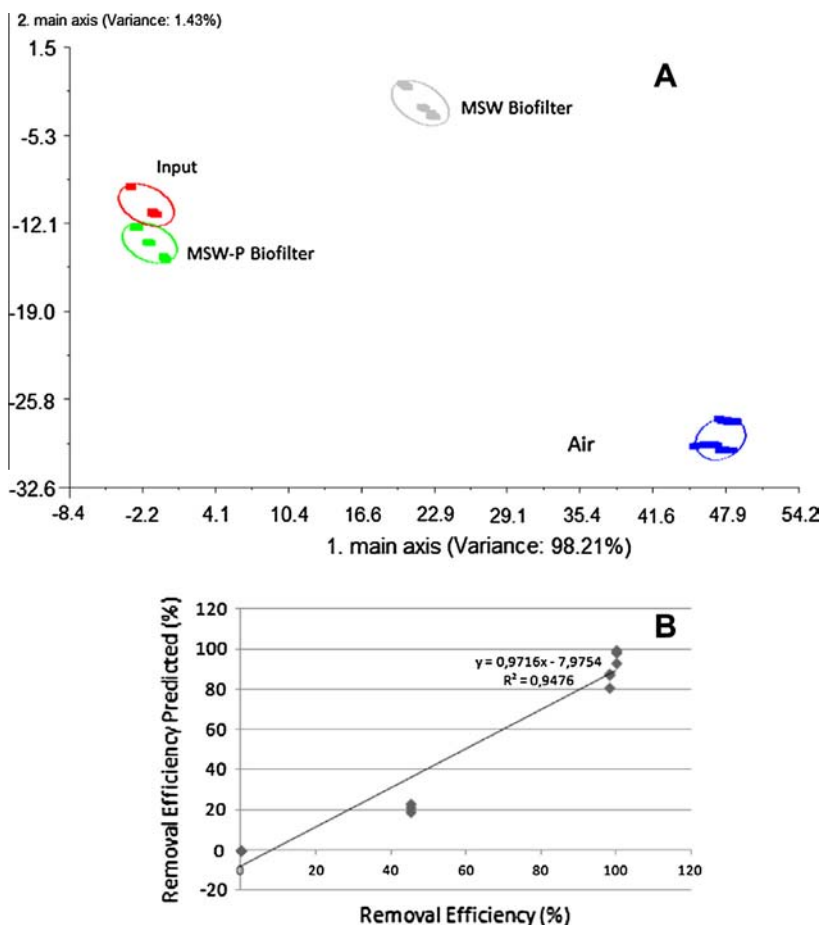


Fig. 8. Principal component analysis (PCA) plots considering Bio1 and Bio2 as the classes in samples (day 88).



**Fig. 9.** (A) Principal component analysis plots considering all the sampling ports and air as the classes in samples (day 223). (B) PLS predicted removal efficiency vs. removal efficiency from e-nose values for combined data sets of day 223.

When the PCA was performed using the sampling ports as the classes, the differentiation between groups was also evident. Fig. 9 A shows the graphic representation of the multivariate analysis carried out on day 223 of the experiment. The moisture content of the biofilters was 57.5% (d.b.) for MSW biofilter and 43.5% (d.b.) for MSW-P biofilter, respectively. The removal efficiency values were similar to those found during the GC/MS analysis (98% MSW biofilter and 45% MSW-P biofilter). The low removal efficiency found in MSW-P biofilter is most likely due to the low moisture content of this material. The inlet concentration of  $\alpha$ -pinene was 7.8 ppm<sub>v</sub> and the output concentrations were 0.2 ppm<sub>v</sub> and 4.3 ppm<sub>v</sub> for MSW and MSW-P biofilter, respectively. The PCA was performed using the e-nose signal response to the samples taken at the inlet, outputs of the biofiltration system and the surrounding air. At the start, 10 metal oxide sensors were included in the multivariate analysis. Based on the parallel loading analysis, which made it possible to check the influence of each sensor on the distribution of data within the PCA-space, specific sensors were eliminated when interference was produced in the PCA. As a result the discrimination power was improved. Similarly, special attention was given to the sensors that influenced the signal response of the samples with a greater concentration of  $\alpha$ -pinene. In Fig. 9A shows this representation were the sensors included in the analysis were (i) hydrogen (W6S), which is selective to hydrogen and breath gases, (ii) the sulfur-organic (W1 W) that is reported to be sensitive to sulfur compounds, but also to many terpenes and sulfur organic compounds and (iii) the methane-aliphatic sensor

(W3S) that is reported react to high concentrations  $\geq 100$  ppm and sometimes is very selective to methane and other aliphatic compounds. The PCA shows a clear differentiation of all the studied classes and seems to be a function of the  $\alpha$ -pinene concentration in the samples. In this sense, the air samples (0 ppm<sub>v</sub>) and the input samples (7.8 ppm<sub>v</sub>) were clearly separated along the  $\chi$  axis, representing 98.21% of the total variance whereas MSW-P biofilter and the input samples are poorly separated between them. Based on the loading analysis observed the differentiations along the  $\chi$  axis was mainly due to the W6S and the W1 W sensors, this indicates that these sensors, related with breath gases, terpenes and smell gases are the cause of the discrimination power obtained. Furthermore, the difference between the classes along the y axis was caused by the W3S signal response, which could be due to the other compounds found in the GC/MS.

The PLS analysis has been also applied to the data sets of day 223, considering the output biofilter, the inlet and the air samples. The signals used to build the PLS regression were those obtained with the sensors chosen during the PCA analysis. The optimal number of latent variables in this model was 3, and  $p$ -value from  $F$ -test was greater than 0.9999, which indicated that model quality is good enough to be used for quantification. Predicted vs. removal efficiencies are shown in Fig. 9B. In this case a linear relationship was obtained with a  $R^2 = 0.95$ , which indicates that the latent variables (comparable with PCA components) described the system and allows to quantify the removal efficiency of the samples correctly.

## 4. Conclusions

Despite the hydrophobic properties of the contaminant ( $\alpha$ -pinene), its moisture content greatly affected the removal efficiency of a biofiltration system using different compost as packing materials. The acclimatisation period necessary to reach high removal efficiency was relatively high (10 days for MSW biofilter and 25 days for MSW-P biofilter), especially when considering that the materials had previously been used to treat gases containing  $\alpha$ -pinene.

The optimal range of moisture content for the packing materials used in this experiment was between 66% and 112% (d.b.) in the case of MSW biofilter and between 51% and 100% (d.b.) in MSW-P biofilter. The last one showed higher removal efficiency during different phases of the experiment, possibly due to the natural affinity of this material with the contaminant. However, it seemed to be more sensitive to moisture changes and more susceptible to moisture losses. This was proven in the phase of the experiment where moisture content was re-adjusted to the lower limit of the optimal range. After low moisture conditions, the acclimatisation period seemed to be longer for both packing materials.

The GC/MS data support the results obtained with the VOC detector in terms of  $\alpha$ -pinene removal efficiencies and did not detect any compound related to a partial degradation of the  $\alpha$ -pinene in the biofiltration system. The e-nose could classify the signal emitted by the biofilters when the  $\alpha$ -pinene concentration was the same, which indicates that there is a natural fingerprint in the outlet depending on the characteristics of each packing material, and also indicates that the e-nose is highly sensitive and has a high discrimination power to small odour nuances. This instrument is able to correctly differentiate different kind of gas samples based on the concentration of  $\alpha$ -pinene in the streams. These results suggest further application of the e-nose as an important tool for the monitoring of biofiltration facilities.

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