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Comparison of the Depuration Efficiency for VOC and Other Odoriferous Compounds in Conventional and Advanced Biofilters in the Abatement of Odour Emissions from Municipal Waste Treatment Plants

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Our work is focused on the characterization and the comparison of the performance of two different types of biofilters: conventional biofilters and advanced biofilters, which in the last years have been succesfully installed in different Spanish large Mechanical Biological Treatment facilities (MBT). Biogenic VOC speciation by HRGC-MS has been performed at the inlet and the outlet of both types of biofilters in order to assess their treatment efficacy regarding odour abatement. Three different sampling and analysis techniques have been applied in this case: a) adsorption of analytes on activated charcoal tubes, and later extraction with CS_2 for GC-MS analysis, b) air sampling with Tedlar bags; SPME extraction of analytes for GC-MS analysis and c) adsorption of analytes on Thermal Desorption Tubes for analysis with an integrated ATD-GC-MS system.
Results demonstrate that advanced biofilters have significantly greater elimination efficiencies than conventional ones.

1. Introduction

Ambient air can contain a complex mixture of substances (which, depending on their nature and concentration, may have possible toxicological and odoriferous implications, among others). These complex mixtures of substances are in part originated by traffic, but also from air emissions from different industrial and agricultural activities and from point and non point emissions from different types of Waste Treatment Plants (WTP) such as Mechanical and Biological Treatment plants (MBT). Due to an increasing public demand for a better air quality, it is observed nowadays that the population requires solutions for odoriferous episodes. Currently, the complaints attributed (in an objective or subjective way) to problems related to bad smells represent a significant percentage of the total air quality complaints (moreover, most of them are related to the activities and emissions of WTPs). The most relevant substances with odoriferous significance which are typically present in the emissions from WTP form very complex mixtures of different compounds, such as sulfur species (hydrogen sulfide, thiols, thioethers), nitrogenated species (ammonia, amines, pyrazines), free short-chain fatty acids, aldehydes, ketones, terpenes and others, as indicated in Mao et al. (2011) and Bianchi et al. (2010).

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The treatment of the organic fraction of Municipal Solid Waste (MSW) is usually carried out by means of one of these three approaches: incineration, biomethanisation or composting. In Spain, the latter two treatment systems are most usually implemented in large facilities known as “Ecoparks”, which are a kind of MBT where composting and/or biomethanisation processes are carried out. Design requirements of these Ecoparks include an adequate ventilation and an absence of fugitive emissions (usually guaranteed by maintaining a negative pressure in all of the buildings and rooms). Therefore, in order to “optimize” the ventilation (economically speaking), gases are often recirculated from one section of the facility to another, thus generating gas currents with very high odoriferous loads. One of the following technologies, or a combination of them, is used for the treatment of WTP emissions with odoriferous loads : chemical or biological scrubbers ("bioscrubber" or "biotrickling"), biofiltration (in the traditional or advanced versions), thermal or catalytic oxidation, oxidation with non-thermal plasma, adsorption on activated charcoal,

Biofiltration is a technology which, as stated by Devinny and Deshusses (1999), has been widely used more or less successfully for longer than 40 years, most commonly in Europe (and more recently in North America and other regions), for the treatment of WTP emissions with high odoriferous significance. These emissions usually have very high flow rates (typically >200,000 ou_E/m^3 in large facilities).

As has been said above, there are two basic types of biofilters: conventional and advanced. The supports used in most conventional biofilters consist principally of mixtures of different proportions of materials and vegetable wastes, such as heather, plugs of wood, roots, bark, coconut fiber... It must be indicated, however, that conventional biofilters, due to the poor characteristics of their biomedia (lower homogeneity of the distribution of microorganism population, non-homogeneous air circulation and support degradation,…), and also because of improper and/or lacking design and maintenance, often cannot fulfill the efficiency requirements needed to reduce or prevent odour problems. These requirements can be highly stringent in those cases where the surroundings of the facility are very vulnerable. Therefore, typical results for the use of conventional biofilters with intensively managed flow rates are: 2-3 year lifespans, outlet concentrations higher than 3,000ou_E/m^3 and odour depuration rates lower than 85 %. This has been the cause that conventional biofiltration has often been thought of as a poor odour removal technology (efficiency-wise), especially when the fact is taken into account that the administrations are starting to require increasingly stringent immission and emission odour concentration limits (VDI 3447:2004).

In order to overcome the limitations of conventional biofilters, advanced biofiltration techniques started to develop during the 90s, achieving much better operative robustness, a longer lifespan (up to 8 years) and a higher depuration efficiency (even greater than > 95 %) and low operational costs. The support of an advanced biofilter consists of two phases: an inorganic and an organic one. The inorganic component contributes a suitable mechanical resistance, whereas the organic phase constitutes an ideal medium for the proliferation and fixation of the microorganisms and acts as an adsorbent, helping to reduce the consequences of variations in the compositions and concentrations of the odorous emission to be treated. The support of advanced biofilters, which is previously sterilized, is inoculated with specific microorganisms of natural origin, which are selected so that they form consortia with proven efficiency for every type of application. Adoption of these advanced biofilters is growing in Spain, where they have been installed in 6 large air treatment facilities (MBTs) since 2002, with a total air treatment capacity near $2 \cdot 10^6$ m^3/h. The results of quarterly efficiency checks of all these advanced biofilters show very high odour removal efficiencies (typically larger than 95 %) and final odour concentrations below 1000 ou_E/m^3.

The goal of the present work is to apply analytical methods to the characterization of the volatile fraction of the gas effluents in order to assess the treatment efficacy of the biofilters and provide guidance for the fine tuning of the operational parameters in order to optimize the treatment performance. Therefore, VOC depuration efficiency was determined in emissions from a conventional biofilter (with peat as biomedia) and from an advanced biofilter (with an organic phase and an inorganic one) installed in two different Ecoparks.

2. Experimental

A total of 48 samples (24 samples from a conventional biofilter and 24 from an advanced one) have been analyzed, 16 with each of three methods, and a VOC screening has been performed for each one. The results of the biofilter inlet and outlet samples have been compared and the elimination efficiencies for several representative compounds have been calculated.

Two sampling techniques were used: a) Sampling in Nalophan bags (which were pre-purged with synthetic air) by means of indirect aspiration and applying a 1:5 v/v dilution with N_2. b) Sampling with commercial activated charcoal cartridges (Orbo 32, Supelco) by aspiration of 40L at a 1 L/min with a calibrated low-flow rate pump (MSA FlowLite).

Three different analytical techniques have been used during this study:

a) Thermal Desorption by means of an Automated Thermal Desorption system (Turbomatrix ATD400, Perkin Elmer): A known amount of Toluene-D8 is added to the Nalophan bag containing the sample, and then a known volume of the diluted sample (500 mL for biofilter inlet samples and 1,000 mL for outlet ones) is transferred, using a 500 mL gas syringe, to the thermally prepurged Thermal Desorption cartridge (CarbopackC/CarbopackB/Carbosieve III, Supelco). The sample is then thermally desorbed at 250ºC and fully transferred to a ThermoTrace HRGC-MS system Thermo Fisher), with a 30 m x 0.25 mm ID BPX-624 column (SGE). Chromatographic conditions were 35 °C (5 min), 5 °C/min up to 250 °C, staying at 250 °C for 10 min. Acquisition was performed in Full-Scan mode (m/z range 35 to 350), and data treatment was carried out using the Xcalibur software (Thermo Fisher) with NIST and Wiley spectra libraries. Quantitation was carried out by relative response to the Toluene-D8 internal standard, using relative response factors for most analytes.

b) Solid-Phase Microextraction (SPME): Gas samples were taken in Nalophan bags of known volume and carried to the laboratory. There, a known amount of Toluene-d8 internal standard was added into the bag, and then, after 15 miz to allow for even diffusion of the internal standard in the bag, a PDMS SPME fiber (Supelco) was exposed to the gas for 45 min after which it was injected into the HRGC-MS system under the previously indicated conditions. Identification and quantitation were performed as indicated above.

c) Activated Charcoal Adsorption: A known volume of gas is pumped through an activated charcoal cartridge. The charcoal is transferred to a vial and desorbed with Carbon Disulfide containing a Toluene-d8 internal standard, prior to injection using an AS2000 autosampler (Thermo Fisher) into the HRGC-MS system with the same conditions as the other techniques. A 5 minute solvent delay is required before the data acquisition begins.

Details of the three applied techniques can be found in Chen et al. (2008), Demeestere et al. (2008) and Jacek et al. (2004).

3. Results

Some of the results of biogenic VOCs that were obtained can be found in the following Table 1 and Figure 1. Regarding the indicated efficiencies, it must be taken into account that, for compounds with outlet concentrations below the detection limit (< 0.01 mg/m^3), a conservative concentration value equal to said detection limit has been used for the calculations. Therefore, the efficiencies reported in Table 1 for these compounds (indicated as “greater than”) must be considered as sub-estimations.

Table 1: Results of VOC analysis by SPME at the inlet and outlet of an advanced biofilter

	Advanced biofilter					Conventional biofilter				
Compounds	Inlet conc. (mg/m^3)	RSD %	Outlet conc. (mg/m^3)	RSD %	Efficiency (%)	Inlet conc. (mg/m^3)	RSD %	Outlet conc. (mg/m^3)	RSD %	Efficiency (%)
1-Propanol	1.6	38.5	<0.01	--	>99	1.3	33.6	0.3	27.1	77
Ethyl acetate	2.4	34.6	<0.01	--	>99	1.8	27.4	1.9	15.3	-6
2-Butanol	0.6	50.0	<0.01	--	>98	0.8	33.9	<0.01	--	99
1-Butanol	1.9	81.4	<0.01	--	>99	1.4	36.1	0.3	30.2	79
Propyl acetate	0.2	93.2	<0.01		>96	0.3	109	0.1	62.6	67
Butanoic acid	0.01	17.7	<0.01	--	>75	0.03	17.7	0.0	37.0	33
Dimethyl disulfide	0.7	--	<0.01	--	>99	0.5	20.2	0.1	11.8	80
3-Methyl-1-butanol	2.3	49.0	<0.01	--	>99	1.9	49.0	0.6	28.5	68
Ethyl butanoate	0.7	112.9	<0.01		>99	0.6	112.9	0.9	19.9	-50
Pentanoic acid	0.3	98.6	<0.01	--	>96	0.6	88.4	0.01	--	98
Propyl propanoate	0.7	69.9	<0.01	--	>99	0.4	69.9	0.1	21.4	88
Butyl acetate	0.1	86.4	<0.01	--	89	<0.01	--	<0.01	--	--
Methyl pentanoate	4	38.9	0.1	6.2	97	3.4	28.7	0.8	17.3	76
Propyl butanoate	1.4	78.0	<0.01	--	>99	1.1	51.3	0.3	36.1	73
Ethyl pentanoate	8.7	4.4	1.4	16.8	84	5.4	16.8	1.1	22.7	80
α-Pinene	1.1	110.1	<0.01	--	>99	0.7	19.9	0.2	42.3	71
Methyl hexanoate	8.2	5.1	2.7	22.6	67	6.0	14.3	1.8	18.2	70
2-β-Pinene	5.8	3.1	2.0	42.6	66	5.1	16.5	0.9	9.2	82
β-Myrcene	2.2	116.3	1.3	39.6	40	<0.01	-	<0.01	--	--
2-Pentylfuran	19.6	91.3	<0.01	--	>99	17.3	44.8	3.6	80.4	79
Ethyl hexanoate	52.6	18.4	10.1	18	81	33.7	27.6	7.4	23.9	78
Limonene	3.1	21.5	0.8	21.7	75	6.4	30.3	1.7	18.0	73
p-Cymene	0.9	98.8	<0.01	--	>99	1.5	--	0.2	62.1	87
Methyl heptanoate	7.8	6.2	<0.01	--	>99	5.2	9.9	1.5	18.9	71
Eucalyptol	0.4	142.3	<0.01		>98	<0.01	--	<0.01	--	--
Hexanoic acid	18.3	84.4	<0.01	--	>99	14.5	94.1	3.2	48.4	78
Propyl hexanoate	5.9	77.3	<0.01	--	>99	5	42.3	1.7	38.9	66
Ethyl heptanoate	3.8	71.6	<0.01	--	>99	3.1	54.3	1.0	33.5	68
Butyl hexanoate	39.1		3.5		92	48.9		8.6		82
Σ Other Terpenes	1.3	37.7	<0.01	--	>99	1.1	24.9	0.3	44.5	73
Odour concentration (ou$_E$/m^3)	18470	23.1	843	21.7	95	20225	28.2	3142	21.4	84,5

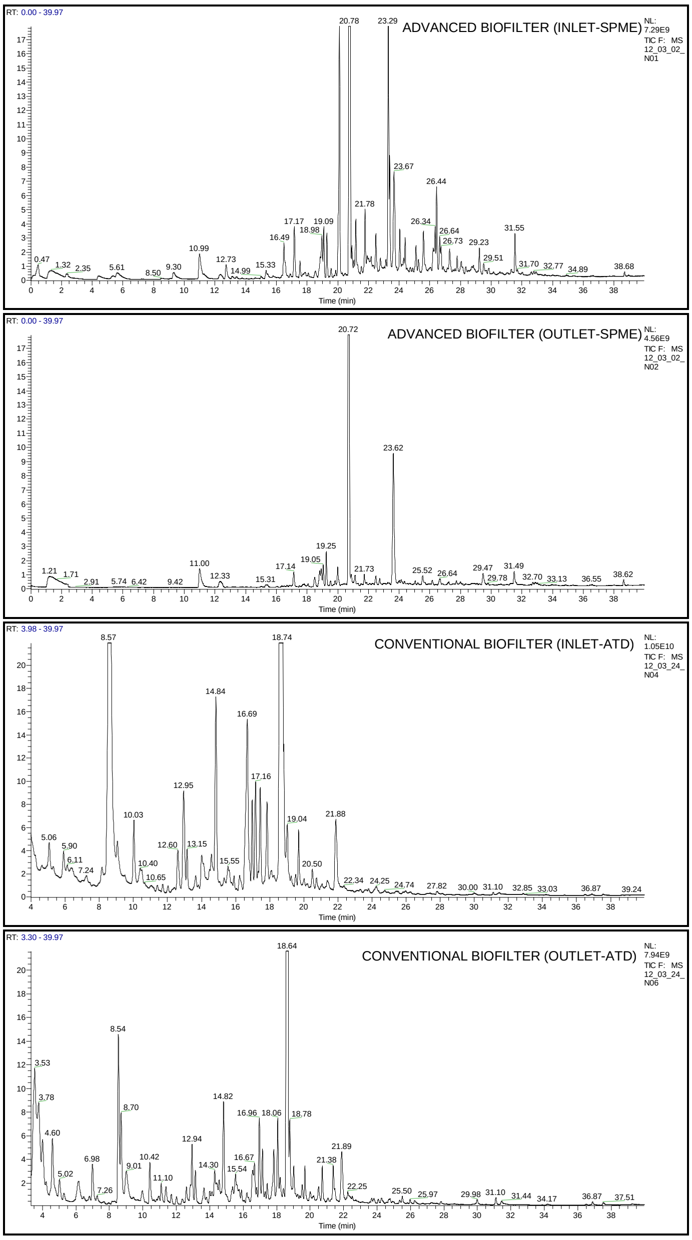

Figure 1: Examples of TIC chromatograms of VOC analyses by different techniques of inlet and outlet samples of an advanced biofilter and a conventional one.

4. Discussion

After evaluating the results obtained during the present work, it can be concluded that:

There are some differences in the results obtained by the three analytical techniques that have been applied: ATD analysis provides better results for the most volatile compounds found at the beginning of the chromatogram, while SPME is more suitable for the heavier compounds found in the middle and later sections of the chromatogram. The results of the response comparison to a Toluene-D8 internal standard achieved the three techniques that have been used are in good agreement, especially in the middle section of the chromatogram, and are quantitatively similar to those found in the literature, such as Font et al. (2011). Some compound classes, however, must be specifically analyzed with one or another technique (i.e.: good results for organic acids, which are highly odoriferous compounds with very unpleasant smells, can be obtained using SPME or ATD, whereas they will not be detected at all when using activated charcoal).

Regarding a comparison between advanced and conventional biofilters, our work has shown that a conventional biofilter with peat support can achieve elimination efficacies ranging between 50 % and 85 %. Advanced biofilters, on the other hand, have consistently higher efficiencies (>95 %) for most biogenic compounds than conventional ones. Moreover, the observed efficiencies are close to those that are typically reported for both types of biofilters regarding odour reduction efficiencies.

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