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BIOFILTRACIÓN DE COMPUESTOS ORGÁNICOS VOLÁTILES UTILIZANDO DIFERENTES TIPOS DE LECHO BASADOS EN MEZCLAS DE COMPOST DE RSU-PODA: MONITORIZACIÓN MEDIANTE DIVERSAS TÉCNICAS

Memoria que presenta
Iván Orlando Cabeza Rojas
para optar al título de Doctor por la Universidad de Sevilla

Sevilla, Abril de 2013

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Memoria presentada por IVÁN ORLANDO CABEZA ROJAS
Para optar al grado de Doctor por la Universidad de Sevilla

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Certifica: Que la presente Memoria de Investigación titulada “Biofiltración de Compuestos Orgánicos Volátiles Utilizando Diferentes Tipos de Lecho Basados en Mezclas de Compost de RSU-Poda: Monitorización Mediante Diversas Técnicas”, presentada por D. Iván Orlando Cabeza Rojas para optar al Título de Doctor por la Universidad de Sevilla, ha sido realizada en el Departamento de Protección del Sistema Suelo, Planta, Agua , bajo la dirección del Dr. D. Rafael López Núñez, reuniendo todas las condiciones exigidas a los trabajos de Tesis Doctorales.

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Fdo: D.José Manuel Pardo Prieto.

ÍNDICE

SUMMARY

Composting is one of the most successful biological processes for the treatment of the residues enriched in putrescible materials. The optimization of parameters which have an influence on the stability of the products is necessary in order to maximize recycling and recovery of waste components. The influence of the composting process parameters (aeration, moisture, C/N ratio, and time) on the stability parameters (organic matter, N-losses, chemical oxygen demand, nitrate, biodegradability coefficient) of the compost was studied. The composting experience was carried out using Municipal Solid Waste (MSW) and Legume Trimming Residues (LTR) in 200 L isolated acrylic barrels following a Box-Behnken central composite experimental design. Second-order polynomial models were found for each of the studied compost stability parameter, which accurately described the relationship between the parameters. The differences among the experimental values and those estimated by using the equations never exceeded 10% of the former. Results of the modelling showed that excluding the time, the C/N ratio is the strongest variable influencing almost all the stability parameters studied in this case, with the exception of N-losses which is strongly dependent on moisture. Moreover, an optimized ratio MSW/LTR of 1/1 (w/w), moisture content in the range of 40-55% and moderate to low aeration rate (0.05-0.175 L_{air} kg^{-1} min^{-1}) is recommended to maximise degradation and to obtain a stable product during co-composting of MSW and LTR.

On the other hand, the concentration of volatile organic compounds (VOCs) during the composting of kitchen waste and pruning residues in a pilot plant, and the abatement of VOCs by different compost biofilters was studied. VOCs removal efficiencies greater than 90% were obtained using composts of municipal solid waste (MSW) or MSW-pruning residue as biofilter material. An electronic nose identified qualitative differences among the biofilter output gases at very low concentrations of VOCs. These differences were related to compost constituents, compost particle size (2-7 or 7-20 mm), and a combination of both factors. The total concentration of VOCs determined by a photoionization analyser and inferred from electronic nose data sets were correlated over an ample range of concentrations of VOCs, showing that these techniques could be specially adapted for the monitoring of these processes.

Finally, 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 α-pinene (a dominant volatile organic compounds (VOC) emitted during the MSW- P co-composting) and Methyl ethyl ketone (MEK). 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). Results indicated that removal efficiencies for both kinds of biofilters were greater than 90% at different stages of the experiment. The acclimatization periods were 10 and 25 days for the MSW biofilter and MSW-P biofilter, respectively in the experiment with α-pinene and 14 days for both biofilters when the MEK was the contaminant present in the air stream to treat. Removal efficiency of the system was strongly dependent upon the moisture content of the packing materials, but the nature of the contaminant (hydrophilic or hydrophobic) plays an important role in the degradation. As moisture content in the biofilters fell to below 66% (dw) for the MSW and 51% (dw) for MSW-P, the removal efficiency decreased to less than 90% when the contaminant was an hydrophobic volatile organic compound (α-pinene). In the case of MEK, the optimal range of moisture content for the packing materials used in this experiment was between 21.5 and 67.5 % (d.w) in the case of the MSW biofilter and between 25.7 and 91.8 % (d.w) for MSW-P biofilter. E-nose and GC/MS data indicate a complete degradation of the α-pinene and MEK by biofiltration, although the e-nose did detect background emissions, characteristic of each type of biofilter. Also, was possible to obtain information about the performance of the biofiltration system in different stages of the experiment. Results suggest that e-nose's will become a more powerful tool for monitoring VOC compounds in biofiltration and composting processes in the future.

1. INTRODUCCIÓN

1.1. PROBLEMÁTICA DE LOS RESIDUOS

La gestión de los residuos se ha convertido en un problema ambiental de alta prioridad en las sociedades industriales que requiere la intervención por parte del estado para su correcta regulación. De esta forma, según la Ley 22 de 2011; Residuo se define como cualquier sustancia u objeto que su poseedor deseche o tenga la intención o la obligación de desechar. Hasta hace relativamente poco tiempo, se empleaban exclusivamente métodos de eliminación de los residuos sólidos como la acumulación en vertederos controlados y la incineración, que negaban de facto el posible valor de los mismos y favorecían la aparición de subproductos tales como lixiviados, partículas sólidas y gases nocivos sin ningún tipo de control. En la actualidad, según las directrices comunitarias y nacionales se prioriza la prevención, es decir la minimización en el origen reduciendo a su vez el impacto generado por la producción de todo tipo de residuos (Herva & Roca, 2013) (Figura 1.1).

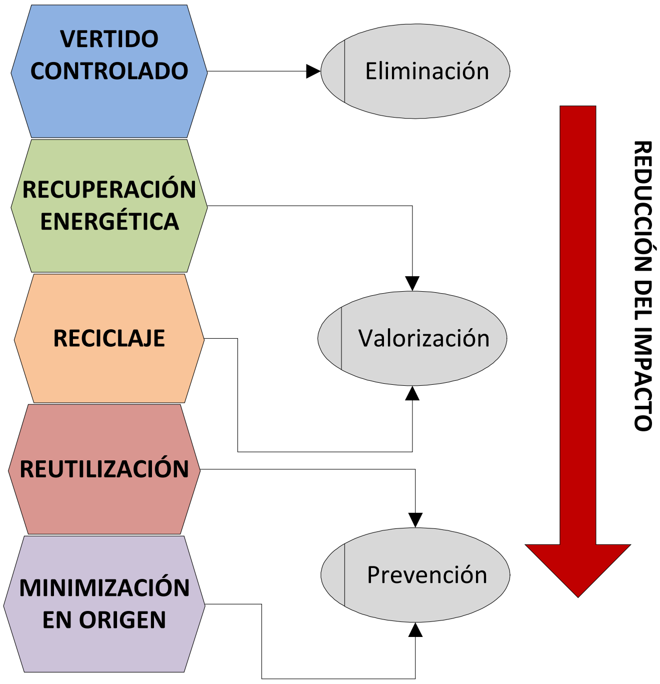

Figura 1.1. Prioridades en la gestión de Residuos

Por lo tanto, las políticas de gestión de residuos de la UE tienen como objetivo reducir los impactos ambientales y sanitarios de los residuos, mejorando la eficiencia del uso de los recursos en Europa. El objetivo a largo plazo es convertir al continente en una sociedad del reciclado, evitando el desperdicio y el uso de los residuos como un recurso inevitable siempre que sea posible.

Sin embargo, a pesar de estas directrices, en Europa las cifras de utilización de recursos y generación de residuos siguen siendo importantes. Todo esto en función de las diversas condiciones económicas y sociales y a los niveles de concienciación ambiental de los diferentes países del continente.

Para resumir, en 2008, los países de la UE-27 generaron cerca de 2.62 billones de toneladas de residuos, lo que supone una media de 5.2 toneladas por persona. En la Figura 1.2 se presenta la generación total de los residuos en el espacio europeo conformado por los 27 países miembros, clasificado según la actividad económica generadora. Es claro que los sectores más importantes en términos de cantidades generadas son la construcción, representando 859 millones de toneladas y la minería con 727 millones de toneladas, teniendo a su vez un mayor impacto potencial en el medio ambiente (Eurostat, 2011). En este contexto cabe anotar, que los residuos urbanos constituyen una fracción minoritaria del total sin ser esta despreciable.

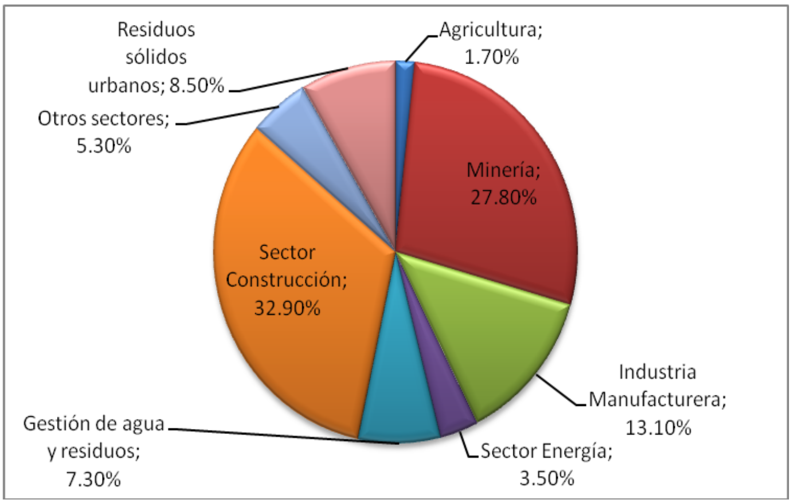

Figura 1.2. Generación total de residuos en UE-27 por actividad económica en 2008 (Eurostat)

El sistema económico de los países desarrollados hace que el 20% de la población mundial consuma el 80% de los recursos (World WildLife Fund WWF). Son precisamente estas diferencias en las estructuras económicas de los países los que crean una importante variación en las cantidades de residuos generados. El rango de variación va desde 660 kg/cap en Letonia hasta 37528 kg/cap en Bulgaria en 2008. Por su parte, España generó 149 millones de toneladas de residuos en este mismo año, lo que implica una producción per cápita de 3500 kg/cap (Eurostat, 2011).

Las estadísticas anteriores indican claramente que la gestión de los residuos en Europa debe ser una prioridad y por lo tanto las autoridades deben continuar fomentando políticas claras que van desde la concienciación de la ciudadanía hasta la optimización de los diferentes procesos de tratamiento de los mismos.

1.1.1. RESIDUOS SÓLIDOS URBANOS

Los Residuos Sólidos Urbanos (RSU) se definen como los generados en los domicilios particulares, comercios, oficinas y servicios, así como todos aquellos que no tengan la calificación de peligrosos y que por su naturaleza o composición puedan asimilarse a los producidos en los anteriores lugares o actividades.

La Ley 22 de 2011 hace distinción entre:

- *Residuos domésticos*: Residuos generados en los hogares como consecuencia de las actividades domésticas. Se consideran también residuos domésticos los similares a los anteriores generados en servicios e industrias. Se incluyen también en esta categoría los residuos que se generan en los hogares de aparatos eléctricos y electrónicos, ropa, pilas, acumuladores, muebles y enseres así como los residuos y escombros procedentes de obras menores de construcción y reparación domiciliaria. Tendrán la consideración de residuos domésticos los residuos procedentes de limpieza de vías públicas, zonas verdes, áreas recreativas y playas, los animales domésticos muertos y los vehículos abandonados.

- *Biorresiduos*: Residuo biodegradable de jardines y parques, residuos alimenticios y de cocina procedentes de hogares, restaurantes, servicios de restauración colectiva y establecimientos de venta al por menor; así como, residuos comparables procedentes de plantas de procesado de alimentos.

En la última década el crecimiento económico de España estuvo acompañado de un aumento de la generación de residuos sólidos urbanos (Eurostat, 2011). En el año 2009, según datos de la fuente estadística europea Eurostat, la generación de residuos urbanos en España se situó en 25.090.000 t, lo que representa una producción de 547 kg/hab, superando la media europea de 513 kg/hab.

Por comunidades autónomas durante 2010, Islas Balears, Canarias y Andalucía registraron los mayores valores per cápita de residuos mezclados[1] (con 630,1 kg., 590,5 kg. y 521.9 kg, respectivamente). En el extremo opuesto se situó la Comunidad de Navarra con 308,3 kg (INE, 2010).

Por otra parte, el análisis autonómico refleja que Cataluña con 1.070.380 t, fue la comunidad autónoma con mayor cantidad de residuos urbanos recogidos

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[1] Residuos mezclados: Se definen como aquellos residuos y enseres domésticos generados en los domicilios particulares, comercios, oficinas y servicios, o en la limpieza de las vías públicas. Estos residuos no se separan en origen.

selectivamente[2], seguidas de las comunidades de Madrid y Andalucía, las cuales reportaron cantidades superiores a 300000 t. (MARM, 2011)

1.1.1.1. Composición de los Residuos Sólidos Urbanos

La correcta gestión de los residuos sólidos urbanos depende directamente de la composición de los mismos. Esta composición varía en función de tres factores, el nivel de vida de la población, la actividad desarrollada por esta y la climatología propia de la región. Por lo que es claro que existe una relación entre la composición de los residuos sólidos urbanos y el poder adquisitivo de cada colectividad (Thitame et al., 2010). En el caso particular de la UE, la evolución experimentada por la sociedad ha hecho que los residuos orgánicos, tradicionalmente la fracción mayoritaria, hayan dado paso a nuevos productos procedentes principalmente de los embases y embalajes. En España, la tendencia de los productos que conforman la producción de los residuos sólidos urbanos se observa en la Figura 1.3.

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[2] Residuos recogidos selectivamente: Son el resultado de la recogida diferenciada de materiales orgánicos fermentables y de materiales reciclables, así como cualquier otro sistema de recogida diferenciada que permita la separación de los materiales valorizables contenidos en los residuos. No incluyen residuos recuperados en las plantas de triaje y clasificación.

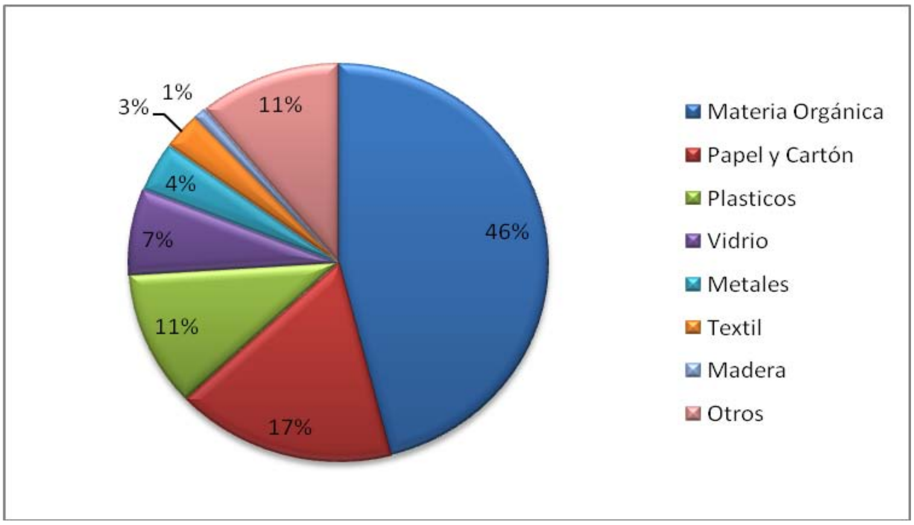

Figura 1.3. Composición RSU en España 2009 (INE, 2010)

A continuación se describen los principales componentes de los residuos sólidos urbanos en España

- *Materia Orgánica:* A pesar de la disminución que conlleva el desarrollo de la sociedad, continúa siendo el principal componente de los residuos. Proviene de los restos de alimentos y de las actividades vinculadas a la jardinería principalmente.

- *Papel y Cartón:* La recogida en origen de este componente ha experimentado un importante incremento. Algunos ejemplos son los periódicos, las cajas, embalajes de cartón, etc.

- *Plástico:* Se encuentra en forma de envases, embalajes, piezas de carrocería de coches y elementos de diversa índole. Debido a su versatilidad, bajo coste, facilidad de producción y resistencia a los factores ambientales es usado en diversos sectores industriales en la fabricación de una amplia gama de productos.

- *Vidrio:* La cantidad de este componente de los residuos urbanos recogida fue de 804000 t durante el 2010, lo que equivale a 17.1 kg/cap (INE, 2010).
- *Textil:* Durante el 2010 se recogieron 4.700 t de este material en España (INE, 2010)
- *Metales:* La hojalata, empleada en el sector alimentario e industrial, es el principal compuesto derivado del hierro que se encuentra en los residuos urbanos. A su vez, el aluminio, utilizado en los botes de bebidas carbonatadas y en los tetra-brik, es por su parte el material no férrico de mayor abundancia.
- *Maderas:* Constituyen partes de mobiliario fundamentalmente. En España durante 2010 se produjeron 192.100 t de este tipo de residuos (INE, 2010).
- *Otros:* Este grupo tiene una composición heterogénea y por la naturaleza de algunos de sus componentes es digno de una atención especial por ser considerados residuos peligrosos.

1.1.1.2. Tratamiento de los Residuos Sólidos Urbanos

La eliminación de los residuos sólidos urbanos (RSU) es uno de los problemas más importantes y controvertidos que enfrentan los gobiernos locales a nivel mundial (Assamoi & Lawryshyn, 2012). Como se ha mencionado anteriormente, el aumento de la generación de residuos debido al crecimiento demográfico, los cambios sociales de estilo de vida, el desarrollo y el consumo de productos menos biodegradables, han llevado a que la gestión y tratamiento de los RSU en varias ciudades de todo el mundo sea un verdadero reto (Asase et al., 2009).

La gestión y destino final de los residuos puede causar diversos efectos sobre la salud y el medio ambiente. Una buena gestión puede proteger la salud pública y la calidad del medio ambiente, contribuyendo a la conservación de los recursos naturales y la economía. A su vez, el abandono o la gestión inadecuada de los residuos producen impactos notables, generando contaminación en el agua, aire, suelo, contribuyendo al cambio climático y afectando a los ecosistemas y a la salud humana. La gestión de los residuos es considerado un indicador mixto ya que contiene variables de presión (vertido de residuos) y de respuesta (valorización de residuos) (OSE, 2011).

Cuando se habla de gestión de residuos sólidos urbanos es necesario diferenciar la etapa de recogida y la etapa de tratamiento posterior y/o eliminación, ya que la segunda etapa está fuertemente condicionada por el grado de selectividad de las operaciones de recogida. Sin embargo, actualmente gran parte de los residuos sólidos urbanos sigue eliminándose sin ningún tipo de aprovechamiento en vertederos (Figura 1.4). Según datos de Eurostat, en España durante el año 2009, se depositaron en vertedero 285 kg/cap frente a los 191 kg/cap de la UE-27.

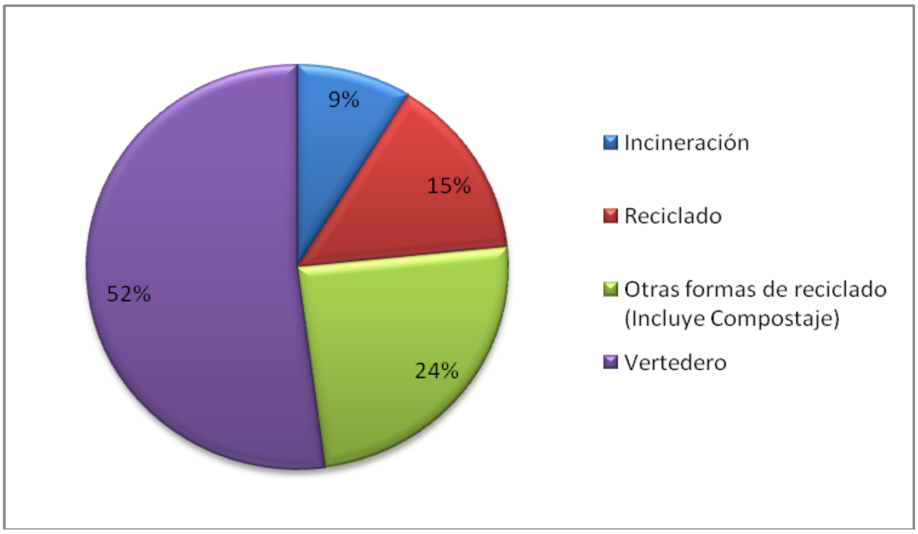

Figura 1.4. Gestión de residuos en España año 2009 (MARM, 2011)

Una parte de la fracción orgánica de los residuos sólidos urbanos aunque mezclada con otros residuos, se destina a instalaciones de tratamiento mecánico-biológico (compostaje o biometanización). En España en el año 2009, se trataron 9.108.845 t de residuos sólidos urbanos en instalaciones de triaje y compostaje y 3.393.374 t en instalaciones de triaje, biometanización y compostaje (OSE, 2011).

El compostaje es una de las formas de valorización de los residuos más empleada y que requiere especial interés (Iqbal et al., 2010; Saha et al., 2008). En el año 2008 se registraron en España, 66 instalaciones de triaje y compostaje distribuidas mayoritariamente en Andalucía. En conjunto con la Comunitat Valenciana y Comunidad de Madrid fueron las que destinaron una mayor cantidad de residuos urbanos a la producción de compost. Cabe anotar que solo un 25% del material de entrada en estas instalaciones fue recuperado y que se utilizó fracción orgánica de recogida selectiva junto con materia orgánica procedente de la fracción de residuos mezclados, lo que supone la obtención de un compost de mala calidad, con usos restringidos (MARM, 2011).

La otra opción de tratamiento mecánico-biológico es la que se lleva a cabo en instalaciones de triaje, biometanización y compostaje. En España se registraron durante el 2008, 15 instalaciones, presentes la mayoría en Castilla y León y Cataluña, las cuales recuperaron el 34.5 % de los residuos de entrada (MARM, 2011).

Otro tipo de valorización de los residuos es la incineración con recuperación energética. En la cual los residuos son quemados para producir energía y calor. Sin embargo, presenta muchas desventajas como altos coste de montaje y operación, producción de emisiones contaminantes y formación de cenizas en cuya eliminación siguen participando los vertederos tradicionales (Assamoi & Lawryshyn, 2012; Lam et al., 2010; Yang et al., 2012). En España durante el 2009 se incineraron 48 kg/cap de residuos con una tendencia al alza durante el periodo 1995-2009. Al mismo tiempo, la UE-27 valorizó en este mismo año 102 kg/cap de residuos utilizando la técnica de incineración (OSE, 2011).

A su vez, es importante tener en cuenta que si no se suman esfuerzos en la optimización de los diversos procesos de tratamiento, los problemas asociados a la producción y la disposición de los residuos pueden persistir. Por lo que los esfuerzos de la comunidad científica deben centrarse en la minimización de los efectos asociados al tratamiento de los residuos sólidos humanos como (Chen, 2010; Ragazzi et al., 2011; Rigamonti et al., 2010):

1. Contaminación de suelos.
2. Contaminación de acuíferos por lixiviados.
3. Contaminación de las aguas superficiales.
4. Emisión de gases de efecto invernadero.
5. Creación de focos infecciosos. Proliferación de plagas de roedores e insectos.
6. Producción de malos olores.

Sin embargo, a pesar de todos los esfuerzos realizados en los diversos tratamientos utilizados en la gestión de los residuos sólidos urbanos, múltiples trabajos concluyen que energética y ambientalmente hablando la mejor solución es el reciclaje y la concienciación de la comunidad sobre el problema (Rigamonti et al., 2010).

1.2. EL COMPOSTAJE Y EL COMPOST

1.2.1. PROCESO DE COMPOSTAJE

El compostaje es definido como la descomposición biológica y estabilización de sustratos orgánicos, bajo condiciones que permiten el desarrollo de temperaturas termófilas como resultado del calor producido biológicamente, con el fin de producir un producto final que es estable, libre de patógenos y semillas de plantas, el cual puede ser beneficiosamente aplicado al suelo (Haug, 1993). En términos técnicos, se puede decir, que el proceso de compostaje consiste en la degradación de la materia orgánica mediante su oxidación y la acción de diversos microorganismos presentes en los propios residuos (Figura 1.5).

$$\boxed{\begin{aligned} &\text{Materia Orgánica} + O_2 \xrightarrow{\text{Microorganismos}} \text{Compost} + \text{Células nuevas} + CO_2 + H_2O + COV \\ &\qquad + NH_3 + SO_4 + \text{Calor} \end{aligned}}$$

Figura 1.5. Ecuación Bioquímica General del proceso de compostaje.

Hay que tener en cuenta que el proceso de compostaje (Haug, 1993):

- *Es biooxidativo y controlado*: Exige una determinada condición biológica, que lo hace diferente tanto de otros procesos físicos y químicos, como de todos aquellos que no se realicen de forma aeróbica.
- *En él intervienen diversos microorganismos*: Es un proceso microbiológico influido por la naturaleza de los organismos presentes (bacterias, hongos y actinomicetos).
- *Implica sustratos orgánicos heterogéneos en estado sólido*.
- *Requiere una etapa termófila:* Durante esta etapa, ocurre la eliminación de patógenos y se inhibe la producción inicial de fitotoxinas.
- *Debe producir un material orgánico estabilizado:* Un material estabilizado tendrá un alto valor fertilizante para ser empleado en agricultura. La utilización como fertilizante o enmienda en la agricultura del producto resultante del proceso de compostaje de residuos sólidos urbanos es una práctica común en diversos países (Barral et al., 2009; Castillejo & Castelló, 2010; Montemurro et al., 2005; Ostos et al., 2008; Warman & Margarit, 2012).

Es por esta razón, que el proceso de compostaje no debe transcurrir espontáneamente, por el contrario, deben controlarse los parámetros que afectan el proceso con el fin de garantizar la valorización final de los residuos obteniendo un producto de calidad a través de este método de tratamiento biológico (Mokhtari et al., 2011; Petric et al., 2012; Vasarevičius et al., 2011).

El proceso de compostaje está dividido en dos fases fundamentales (Soliva, 2001):

- *Fase de Descomposición:* En esta fase, ocurre la degradación de las moléculas complejas a moléculas orgánicas más sencillas. Es un proceso exotérmico debido a la actividad biológica y está compuesta por dos etapas, etapa mesófila con temperaturas hasta los 45 ºC y una etapa termófila con temperaturas que pueden llegar a los 70 ºC. La monitorización durante esta fase del proceso es importante, condicionando las propiedades del producto final.
- *Fase de Maduración:* Se compone de dos etapas, una denominada enfriamiento con temperaturas que van desde los 40 ºC y una llamada estabilización con una baja actividad microbiana y donde se presenta la aparición de organismos superiores. Esta fase a diferencia de la anterior no requiere especial control ya que la actividad biológica es mucho más reducida y los requerimientos de oxígeno muy inferiores.

1.2.1.1. *Parámetros del Proceso de Compostaje.*

Como se dijo anteriormente, el proceso de compostaje es un sistema complejo en donde los microorganismos cumplen un papel fundamental, por lo que todos los factores que puedan limitar su desarrollo serán limitantes del propio proceso (Barrena-Gomez, 2006).

Aunque los parámetros de control que más influyen en el proceso de compostaje pueden variar dependiendo del tipo de materia prima o sustrato a tratar. Diversos trabajos de investigación han concluido que los más importantes son: La temperatura, humedad y porosidad, pH, aireación y cantidad de nutrientes (Relación C/N) (Delgado-Rodríguez et al., 2010; Madejón et al., 2002; Petric et al., 2012; Yañez et al., 2010). En la tabla 1.1 se describen dichos parámetros.

Tabla 1.1. Parámetros de control del proceso de compostaje (Barrena-Gomez, 2006; Haug, 1993; Soliva, 2001)

PARÁMETROS	**INFLUENCIA EN EL PROCESO**
TEMPERATURA	Proporciona información directa del funcionamiento del mismo (indica incremento en la actividad biológica) El mantenimiento de temperaturas elevadas asegura la higienización del material pero puede inhibir la actividad microbiana, por lo que se debe procurar un equilibrio de temperaturas entre la máxima higienización

	(≥55ºC) y la biodegradación (45-55 ºC).
HUMEDAD Y POROSIDAD	La humedad favorece la población microbiana y hace posible la utilización de las moléculas orgánicas haciéndolas disponibles a los microorganismos. La actividad biológica empieza a disminuir a niveles de humedad inferiores al 40%. Una humedad muy alta con materiales poco porosos produce una disminución en la transferencia de oxígeno, lo que genera zonas anaeróbicas que facilitan la producción de olores, generación de lixiviados y pérdida de nutrientes. Rango óptimo de humedad 40-60% (variable en función de la naturaleza del material) La mezcla de diversos materiales facilita la obtención de la porosidad y humedad adecuadas.
pH	Valores extremos de pH pueden ser perjudiciales para diversos grupos de microorganismos. pH cercanos a 7 al inicio del proceso garantizan la presencia de diversas colonias de microorganismos,

	El pH es a la vez un indicador de la evolución del proceso, disminuye al inicio por la formación de ácidos libres y posteriormente aumenta debido al amoniaco desprendido en la descomposición de las proteínas. Una reducción brusca del pH puede indicar que están ocurriendo reacciones anaeróbicas no deseadas.
AIREACIÓN	La naturaleza aeróbica del proceso la hace indispensable. Los microorganismos consumen oxígeno durante la degradación del material. Relacionada con la temperatura, ya que participa en la producción y la pérdida de calor.
RELACIÓN C/N	Es necesario un equilibrio entre los principales nutrientes para los microorganismos (carbono y nitrógeno). Relaciones C/N altas hacen que el proceso sea lento. Relaciones C/N bajas ocasionan pérdida de nitrógeno. Se estima una relación óptima C/N entre 25 y

	35. Influye en las condiciones de inicio del proceso de compostaje y en su cinética

1.2.2. *EL COMPOST*

Al igual que el proceso de compostaje, no existe un consenso universal en la definición de compost. Sin embargo, la definición más apropiada para este producto es (Haug, 1993): *"Compost es considerado un producto acondicionador orgánico del suelo, el cual ha sido previamente estabilizado, semejante al humus, que está libre de semillas y de patógenos para los humanos y las plantas, es un producto que no atrae insectos, que puede ser manipulado y almacenado sin ningún tipo de molestia y el cual es beneficioso para el crecimiento de las plantas"*

Con respecto a la estabilidad del compost existen diferentes métodos basados en sus propiedades (Barrena-Gomez, 2006; Guo et al., 2012):

- *Métodos Físicos:* Temperatura, oxígeno, color, olor, densidad óptica de los extractos.

- *Métodos Químicos:* Contenido de materia orgánica, relación C/N, demanda química de oxígeno (DQO), contenido en polisacáridos, concentración de sustancias húmicas, etc.

- *Métodos Biológicos:* Índice respirométrico, generación de calor, actividades enzimáticas, ensayos de auto-calentamiento, ensayos de germinación y crecimiento de las plantas.

Una vez se obtiene un producto estable y beneficioso para las plantas, el compost aplicado como enmienda orgánica genera las siguientes ventajas (D'Hose et al., 2012; Nguyen et al., 2012):

- Influye directamente sobre el volumen de los poros, mejorando la distribución de la humedad e intercambio catiónico.
- Aumenta la capacidad de retención hídrica.
- Permite la absorción lenta de los nutrientes que aporta.
- Incrementa la retención de nutrientes por parte de las plantas y de elementos traza en el suelo.
- Previene la erosión de los suelos.
- Aumenta la microflora del suelo.
- Favorece la mineralización de la materia orgánica.

En España, el Real decreto 824 de 2005 establece la clasificación de las enmiendas orgánicas según sus propiedades físicas y químicas y el método de obtención.

1.3. ACTIVIDADES QUE CAUSAN EMISIÓN DE OLORES

Olor se define como *la propiedad de una sustancia química o mezcla de sustancias que en función de su concentración reacciona sobre el sentido del olfato y por lo tanto es capaz de causar una sensación de olor* (Bidlingmaier & Müsken, 2007).

Debido a que el olor es un parámetro que no puede ser medido física o químicamente, es decir es un parámetro única y exclusivamente sensorial, los seres humanos lo perciben de diferentes maneras, siendo función de influencias culturales y personales como la educación y las experiencias vividas por el individuo (Bidlingmaier & Müsken, 2007).

Ciertas condiciones deben cumplirse antes de que una sustancia pueda crear un olor:

- *Volatilidad*: Las moléculas odoríferas en condiciones normales deben estar en el aire antes que produzcan un estímulo en el sentido del olfato.
- *Solubilidad en agua*: La membrana mucosa del olfato tiene una capa de agua que hace más fácil que la sustancia penetre en la misma si es soluble en agua.
- *Solubilidad en grasas:* La capa de grasa de las células nerviosas puede ser penetrada únicamente por sustancias solubles en la misma.
- *Polaridad:* La intensidad de la polaridad es decisiva para la percepción de los olores. Debe ser moderadamente acentuada.

La emisión de olores está asociada particularmente a un determinado grupo de industrias y actividades específicas. El anexo 3 del Anteproyecto de Ley contra la Contaminación Odorífica de la Generalitat Catalana, define los valores objetivos de inmisión para un determinado conjunto de actividades de procesamiento, transporte y disposición. Estas actividades son:

- Actividades ganaderas y tratamiento de sus productos y residuos.
- Plantas de colección, bombeo, transporte y tratamiento de aguas residuales y sus lodos.
- Plantas de tratamiento y disposición de residuos urbanos.
- Industrias cerveceras.
- Celulosas.
- Industrias de productos químicos, tratamiento y secado de vegetales, etc.

En Andalucía, la emisión de olores es regulada en el recientemente aprobado Decreto de Calidad del Aire (Decreto 239 de 2011). Este texto considera los olores como un contaminante y formula los requerimientos necesarios para conceder una autorización ambiental integrada o autorización ambiental unificada a las actividades potencialmente emisoras de olores al medio ambiente en el marco de la Ley de Gestión Integrada de la Calidad Ambiental (GICA).

Es claro que las actividades de tratamiento biológico de residuos sólidos urbanos como el compostaje son procesos susceptibles a la generación de olores que afecten a los trabajadores y la comunidad en general (López et al., 2011).

1.3.1. OLORES EN PLANTAS DE COMPOSTAJE DE RESIDUOS SÓLIDOS URBANOS

Una de las principales amenazas del éxito operativo de la mayoría de instalaciones de compostaje es el potencial inherente del proceso de crear olores desagradables, así como, la generación de polvo y el favorecer la presencia de insectos, aves y roedores. Aunque todos estos problemas pueden ser mermados con el correcto control de las variables operacionales del proceso como por ejemplo, la humedad (en el caso del polvo), el aseguramiento de la fase termófila (destrucción de los huevos de insecto), el correcto manejo de las materias primas del compostaje especialmente cuando se trabaja con residuos sólidos urbanos y el aseguramiento de las condiciones aerobias del proceso (Evita la formación de algunos compuestos que generan mal olor (Stoffella & Kahn, 2005)). El control de los olores es indudablemente el problema más difícil de controlar en la práctica del compostaje (Haug, 1993).

La emisión de olores se inicia normalmente con la recepción de las materias primas del proceso (residuos) a la planta de tratamiento y sobre todo en las fases iniciales del compostaje. A su vez, en el caso de producirse condiciones anaeróbicas en el proceso, debido al escaso control de la aireación, se producirán compuestos de azufre de olor intenso. De la misma forma, una degradación aeróbica incompleta producirá emisiones de alcoholes, cetonas, ésteres y ácidos orgánicos; Por otra parte, un balance de nutrientes equivocado puede dar lugar a emisiones de compuestos orgánicos volátiles y amoniaco (Bianchi et al., 2010).

Existen diversos compuestos generadores de olor emitidos por las plantas de tratamiento de residuos. En la Tabla 1.2 se resumen los principales compuestos detectados en dichas instalaciones.

Tabla 1.2. Grupo de compuestos emitidos en plantas de tratamiento de residuos (Bidlingmaier & Müsken, 2007; Delgado-Rodríguez et al., 2011; Haug, 1993; Kumar et al., 2011; Mao et al., 2006; Pierucci et al., 2005; Tsai et al., 2008a)

COMPUESTO	**CARÁCTER**	**UMBRAL (µg m^{-3})**	
		Bajo	**Alto**
Compuestos de Azufre			
Sulfuro de hidrógeno	Huevos podridos	0,7	14
Oxisulfuro de carbono	Picante		
Disulfuro de carbono	Desagradable	24	23000
Sulfuro de dimetilo	Col podrida	2,5	50,8
Disulfuro de dimetilo	Sulfuro	0,1	34,6
Trisulfuro de dimetilo	Sulfuro	6,2	6,2
Metanotiol	Sulfuro picante	0,04	82
Etanotiol	Sulfuro, a tierra	0,032	92
Compuestos de Nitrógeno			
Amoniaco	Picante, penetrante	26,6	39600

Aminometano	Pescado picante	25,2	12000
Dimetil amina	Pescado, amina	84,6	84
Trimetilamina	Pescado, picante	0.8	1
3.metinildol (escatol)	Heces	$4\ 10^{-5}$	268
Ácidos Grasos volátiles			
Metanoico	Penetrante, picante	45	37800
Etanoico	Vinagre	2500	250000
Propanoico	Rancio picante	84	60000
Butanoico	Rancio	1	9000
Pentanoico	Desagradable	2,6	2,6
3-metil butanocio	Rancio	52,8	52,8
Cetonas			
Propanona	Frangante, mentol	47500	$1{,}6\ 10^{6}$
Butanona	Fragante, acetona	737	147000
2-Pentanona	Fragante	28000	45000
Otros			
Benzotiazol	Penetrante	442	2210
Etanol	Frangante, hierba	0,2	4400
Fenol	Medicinal	178	2240
Umbral bajo: Menor límite de detección para las personas más sensibles **Umbral alto: Límite de detección para la mayor parte de las personas**			

Los Compuestos Orgánicos Volátiles (COVs) generados en las plantas de compostaje son la principal causa de los malos olores generados en las mismas. Estos malos olores, producen diversas molestias en los alrededores de las zonas de tratamiento y pueden tener efectos adversos en la salud de los trabajadores de las plantas y en los vecinos (Baldwin et al., 1999). Estos COVs provienen fundamentalmente de la degradación microbiana de los residuos y restos de plantas, las cuales son las principales materias primas del proceso. (Müller et al., 2004).

Los Compuestos Orgánicos Volátiles se definen como cualquier compuesto que contiene carbón en su estructura molecular, que tiene una presión de vapor superior a 0.1 milímetros de mercurio (mm Hg) a condiciones normales (20ºC y 760 mm Hg) y que participa en las reacciones fotoquímicas atmosféricas, a excepción del monóxido de carbono, dióxido de carbono, ácido carbónico, carburos metálicos o carbonatos y carbonato amónico. Incluyen una variedad de compuestos químicos que pueden causar efectos a corto y largo plazo en la salud de las personas y son los principales causantes del smog. Por otra parte, los gases inorgánicos son llamados compuestos inorgánicos volátiles (CIVs) e incluyen gases como sulfuro de hidrógeno, dióxido de sulfuro, sulfuro de carbono y amoniaco (Revah & Morgan-Sagastume, 2005). Estos últimos también tienen una influencia importante en la producción de malos olores en las plantas de compostaje.

Diversos estudios han identificado al limoneno, α-pineno y otros terpenos como los COVs más importantes en la generación de olores en plantas de compostaje (Bidlingmaier & Müsken, 2007; Breza-Boruta et al., 2010; Louhelainen et al., 2001). Por otra parte, se ha comprobado que el escaso control de la aireación en los procesos de compostaje favorece la aparición de zonas anaeróbicas y la formación de compuestos de azufre como: ácido sulfhídrico, metanotiol, sulfuro de dimetilo y disulfuro de dimetilo, entre otros (Pierucci et al., 2005; Staley et al., 2006; Tsai et al., 2008b). El riesgo de formación de estos compuestos es mayor en las primeras fases del proceso y durante el almacenamiento de los residuos orgánicos debido a las condiciones de humedad de los materiales y a que porciones importantes de sustancias orgánicas fácilmente degradables son descompuestas (Bidlingmaier & Müsken, 2007; Tsai et al., 2008b).

Con respecto al grupo de las cetonas, la 2-butanona puede ser el compuesto más importante perteneciente a este grupo funcional y emitido en los procesos de compostaje y puede ser considerado uno de los compuestos que influye más significativamente en la producción de los olores (Delgado-Rodríguez et al., 2011).

1.3.1.1. Efectos de los olores en la salud

Los trabajadores de las plantas de compostaje están inevitablemente expuestos a los COVs que generan el olor en dichas instalaciones. Estos compuestos pueden producir trastornos secundarios como náuseas y vómitos, reacciones de hipersensibilidad e incluso alteraciones de tipo respiratorio (Schiffman & Williams, 2005). Los efectos más significativos de los COVs son de tipo tóxico sistémico, entre los que cabe destacar trastornos renales, hematológicos, neurológicos, hepáticos e irritaciones mucosonasales (Mücke & Lemmen, 2012).

Es importante resaltar que las consecuencias de la inhalación dependen directamente de la concentración de los COVs que entran al sistema olfativo del afectado. Sin embargo, diversos estudios reflejan que en las fases iniciales del proceso, la concentración de los compuestos orgánicos volátiles detectados supera ampliamente la concentración umbral olfativa, en algunos casos en unas 20000 veces como es el caso del limoneno y en unas 3000 veces como es el caso del pineno (Tolvanen & Hänninen, 2007).

1.4. MÉTODOS DE CONTROL DE LOS OLORES

Una de las dificultades más importantes en el caso de la gestión y mitigación del olor es que es un rasgo subjetivo y bastante variable. Cabe anotar que aunque en la actualidad se han alcanzado avances significativos en la cuantificación del olor y de los compuestos químicos que lo ocasionan, siempre existirá una amplia variación entre la percepción de la gente ante el mismo fenómeno oloroso (Stoffella & Kahn, 2005).

En España, como se mencionó anteriormente, la legislación en el control de olores es relativamente reciente desarrollándose progresivamente por autonomías. En el caso específico de Andalucía, el Decreto 239 de 2011 de la Consejería de Medio Ambiente por el que se regula la calidad de medio ambiente atmosférico, fomenta el interés por parte de los centros de investigación de la comunidad autónoma en unir los esfuerzos en el control de los contaminantes volátiles que causan olor. Por esta razón, la monitorización de los olores, su tratamiento y evaluación de las técnicas más utilizadas hasta el momento son un tema de gran actualidad.

En el diseño y construcción de un sistema de control de los olores, se debe tener en cuenta que la construcción de un sistema de tratamiento de gases, cuya finalidad es solucionar un problema, no debe acarrear un nuevo impacto ambiental, por lo que los subproductos del sistema de mitigación deben ser estudiados con detenimiento.

En la actualidad existen diversas técnicas para el control de los olores producidos por los COVs y CIVs en la industria. Para seleccionar un método adecuado, es importante considerar las propiedades físicas, termodinámicas y de reactividad de los contaminantes. Entre las propiedades más influyentes en la caracterización de los COVs y la posterior selección del método de control se tienen: La fase (gas o líquido), tipos de enlaces presentes en los compuestos (covalentes o polares), capacidad de ionización, presión de Vapor, solubilidad en agua y reactividad (Morgan-Sagastume & Noyola, 2006).

Las tecnologías de control de compuestos orgánicos volátiles y CIVs se clasifican de acuerdo a la naturaleza del control (Física, Química y Biológica) (Figura 1.6.). Entre las tecnologías más empleadas se encuentran la dilución, condensación, adsorción, combustión, enmascaramiento, scrubbers y la biofiltración.

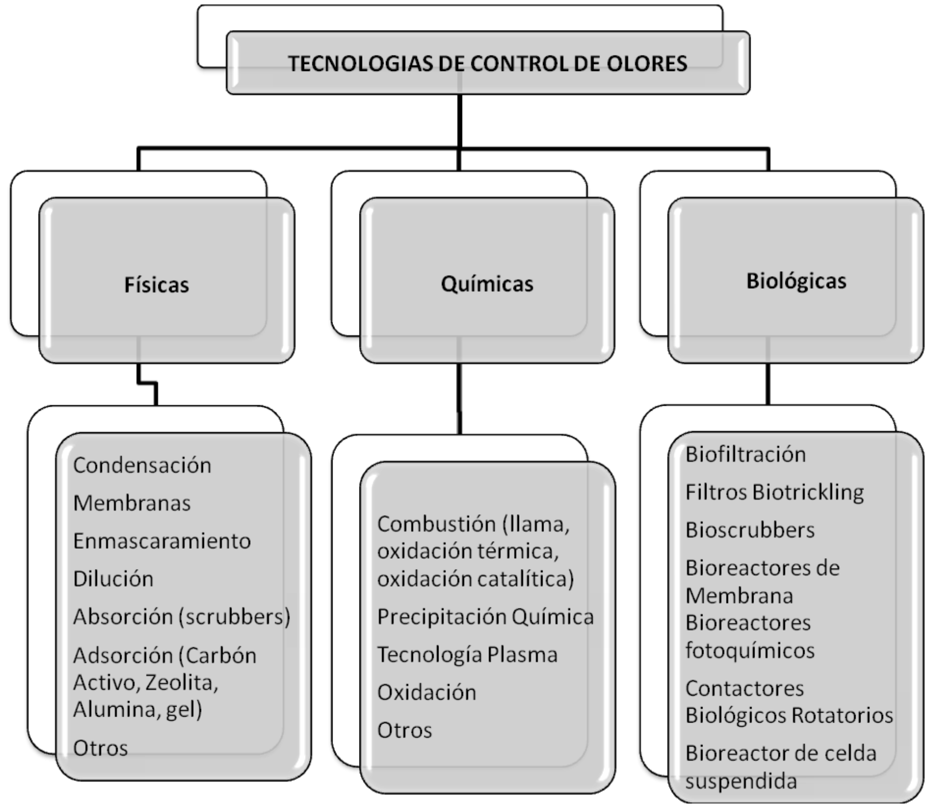

Figura 1.6. Tecnologías de control de olores clasificadas según su naturaleza (Revah & Morgan-Sagastume, 2005).

Es claro que no todos los sistemas son aplicables en todo el intervalo de flujos y concentraciones. Como norma general, la tendencia en instalaciones de tratamiento de efluentes industriales es utilizar instalaciones compactas, de bajo coste y que sean modulares, con lo que proporcionan un fácil manejo y seguimiento de la instalación. De esta forma en la elección de un sistema de tratamiento de gases odoríferos se deben tener en cuenta los siguientes factores:

- Caudal y tipo de caudal.

- Características físico químicas de los gases (composición, partículas, etc,)
- Concentración de compuestos a tratar.
- Espacio necesario para la planta de depuración
- Rendimiento requerido del tratamiento
- Costes de mantenimiento
- Inversión inicial para obra.

En la Figura 1.8. se presenta un esquema de las diversas tecnologías utilizadas en el tratamiento de los compuestos orgánicos volátiles clasificadas según las características de caudal y concentración del efluente gaseoso de interés.

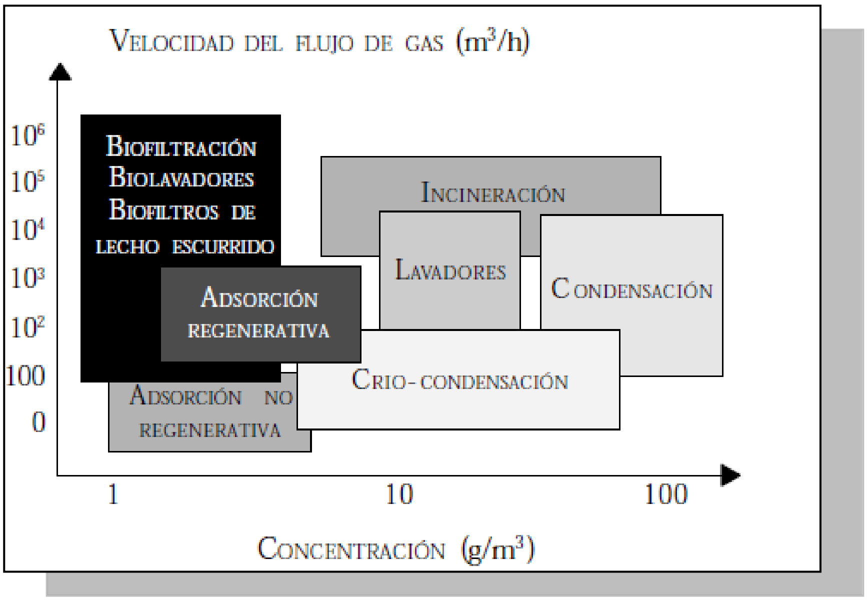

Figura 1.8. Tecnologías para el control del olor clasificadas según concentración y caudal de la corriente gaseosa a tratar (Cardenas Gonzalez et al., 2003).

De la Figura 1.8. se puede concluir que el mecanismo de biofiltración es entonces una de las técnicas de mitigación de olores que representa gran utilidad para el tratamiento de compuestos orgánicos e inorgánicos volátiles a concentraciones y flujos moderados (Dorado et al., 2010; López et al., 2011; Pagans et al., 2005).

Dentro de las principales ventajas de los métodos biológicos se tiene que operan a temperaturas normales (10-40 ºC) y presiones atmosféricas, son menos costosos, simples de operar y ecológicamente limpios comparados con los tratamientos fisicoquímicos. Además, permiten tener eficiencias considerables con concentraciones medias de contaminante y flujos entre 150 y 10000 m3/h (Revah & Morgan-Sagastume, 2005).

1.5. BIOFILTRACIÓN

Las reacciones microbianas han sido utilizadas durante todo el siglo veinte en el tratamiento de aguas residuales y diversas clases de residuos sólidos, pero es desde 1950 cuando esta técnica empezó a ser empleada en el tratamiento de gases contaminados (Pomeroy, 1957). Durante los inicios de esta tecnología se empleaban normalmente sistemas abiertos en los cuales se utilizaba suelo poroso como material de soporte. Después de la publicación de los fundamentos de la tecnología de biofiltración, la misma se difunde principalmente en los Estados Unidos de América y la Alemania Occidental. Posteriormente, todos los esfuerzos por parte de la comunidad científica se centraron en conseguir mayores eficiencias con mayores cargas de compuestos volátiles: Es entonces en 1970 cuando en Alemania y en los

Paises Bajos se consiguieron diseños utilizando nuevos lechos de relleno como mezclas de compost y trozos de madera (Cardenas Gonzalez et al., 2003). Durante la década de 1980, las investigaciones lograron desarrollar sistemas cerrados con algunos sistemas de control automático y materiales filtrantes inertes, junto con modelos matemáticos relacionados con los procesos de biofiltración en general (Ottengraf et al., 1986).

Las investigaciones posteriores en el área han hecho de la tecnología de biofiltración una alternativa bastante versátil en el tratamiento y control de compuestos volátiles ya sean estos compuestos alifáticos, aromáticos, compuestos azufrados, óxidos de nitrógeno, amoniaco, halogenados y no halogenados, etc (Detchanamurthy & Gostomski, 2012; Lee et al., 2013). Las ventajas obtenidas en diversas instalaciones piloto y de laboratorio han ocasionado que la comunidad científica centre también sus esfuerzos en el estudio de diversos materiales filtrantes, analizando las propiedades físicas, químicas y económicas y buscando alternativas de optimización de los mismos. (Dorado et al., 2010).

En la actualidad, los esfuerzos se enfocan en la creación de sistemas con un mejor control de los parámetros de proceso, cinéticas de degradación y modelización de la tecnología y de los diversos fenómenos que están involucrados; Además en la influencia de los parámetros operacionales de un sistema de biofiltración en la eliminación y degradación de los compuestos individualmente (Bagherpour et al., 2005; Morales et al., 2003; Morgan-Sagastume & Noyola, 2006; Roshani et al., 2012). Aunque el mecanismo exacto de eliminación de los compuestos volátiles por parte de los materiales de relleno no es muy conocido, en los últimos años se han hecho esfuerzos considerables en estudiarlos (Pagans et al., 2007).

A su vez, los intentos de optimización de la eficiencia de remoción de la biofiltración en el tratamiento de emisiones con concentraciones altas de compuestos volátiles, han generado investigaciones con resultados interesantes utilizando microorganismos previamente seleccionados y adaptados a escala piloto (Rene et al., 2010; Vergara-Fernández et al., 2005; Vigueras et al., 2009).

1.5.1. *BIOFILTRO*

Biofiltro se define como *un reactor para la conversión de compuestos químicos de la fase gaseosa a productos comunes de una degradación biológica como dióxido de carbono, agua y sales minerales* (Datta & Grant-Allen, 2005) (Figura 1.9).

$$\boxed{\begin{array}{l} COVs\ y\ CIVs + O_2 + H_2O + Nutrientes \\ \xrightarrow[Microorganismos]{} CO_2 + H_2O + Sales\ Inorgánicas + Biomasa\ Muerta + Residuos\ Poliméricos \end{array}}$$

Figura 1.9. Ecuación Bioquímica del proceso de Biofiltración

En términos generales en el biofiltro, el aire contaminado pasa a través de un lecho de medio poroso y húmedo, donde los contaminantes son adsorbidos a la superficie del medio en el que son degradados por microorganismos. La degradación de los contaminantes ocurre previa transferencia del aire a un medio líquido en donde es utilizado como fuente de carbono y energía, en el caso de los compuestos orgánicos, o como fuente de energía, en el caso de los compuestos inorgánicos (Figura 1.10). Este proceso implica producción de biomasa y oxidación parcial o total del contaminante. De esta manera, los procesos de biofiltración dan lugar a una descomposición completa de los contaminantes, creando productos no peligrosos (Cardenas Gonzalez et al., 2003). En realidad, la capacidad de adsorción del medio es relativamente baja, pero dado que existe una oxidación de los compuestos adsorbidos, se regenera la capacidad de absorción. La adsorción es más rápida que la oxidación por lo que se hace necesario un medio con gran capacidad de adsorción para lograr una buena eficacia.

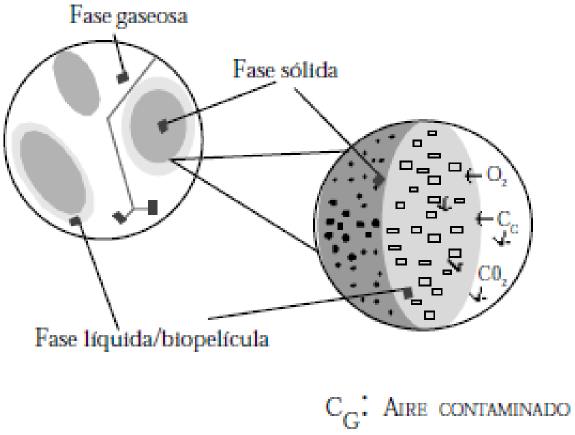

Figura 1.10. Mecanismo de Degradación del Contaminante (Revah & Morgan-Sagastume, 2005).

El tratamiento de los compuestos odoríferos vía biofiltración ha sido el método más común que se ha implantado en las instalaciones de compostaje y en plantas de tratamiento de aguas residuales (Chung, 2007). El material de con el que se hace el biofiltro (medio biológico filtrante) es una mezcla de materiales con un alta área específica y alta cantidad de espacio de aire libre. El recurso más fácilmente disponible (y con gran eficacia) puede ser compost maduro (Luo & Lindsey, 2006). El compost, suelo, turba, restos de poda triturados y corteza, así como materiales inertes que mejoran fundamentalmente las propiedades físicas, se encuentran dentro de los materiales más utilizados como lechos en los biofiltros. Sin embargo, el compost tiene un valor añadido frente a los otros materiales ya que representa la valorización de los residuos empleados en su fabricación y a su vez, en muchos casos, no es necesaria una inoculación previa, ya que este material es rico en microorganismos degradadores de los compuestos contaminantes. El compost y el carbón activo comercial (CAC) han sido evaluados como los materiales más adecuados ante cargas intermitentes de contaminante, teniendo en cuenta propiedades químicas y físicas y parámetros de coste (Dorado et al., 2010). El compost posee la superficie y los nutrientes necesarios para que sobre ella se desarrolle una “biopelícula” de microorganismos que serán los responsables de la degradación de los compuestos indeseables del gas. Una alta cantidad de espacio de aire libre favorece una baja caída de presión del gas así como una adecuada oxigenación del filtro y distribución del flujo de gas (Pagans et al., 2005).

Entre los factores operacionales y fisicoquímicos más importantes a tener en cuenta en el diseño y los cuales afectan directa o indirectamente el rendimiento del sistema de biofiltración se tiene, entre otros, la humedad del lecho, la humedad relativa de la corriente del contaminante a tratar, la temperatura, el pH, el material de soporte del lecho, el tiempo de retención en cama vacía del contaminante en el material de relleno, la concentración del contaminante, la porosidad del lecho, los aspectos nutricionales y microbiológicos del sistema (Leson & Winer, 1991; Mohseni et al., 1998; Morgan-Sagastume & Noyola, 2006; Ottengraf et al., 1986; Streese et al., 2005).

A continuación se detallan las características más importantes de los parámetros fisicoquímicos y operacionales a tener en cuenta en el diseño, montaje y monitorización de un sistema de biofiltración (Datta & Grant-Allen, 2005):

- La actividad de los microorganismos y el crecimiento es óptimo en un intervalo de temperatura entre 20-40ºC (Menard et al., 2011). Una temperatura más alta va a destruir la biomasa, mientras que temperaturas más bajas se traducirá en una menor actividad de los microorganismos. Por lo que en zonas frías, se hará necesaria la calefacción de gas a la entrada. Por el contrario, una temperatura muy alta, puede producir una lisis microbiana (Vergara-Fernández et al., 2012).

- El pH en el medio debe ser cercano al neutro (Tyson et al., 2008). Durante el proceso de compostaje se emiten gases que presentan un pH variable dependiendo de la etapa. Un ejemplo de esto es la aparición de picos básicos procedentes del amoniaco que pueden aumentar el pH del medio. Los lechos utilizados en los sistemas de biofiltración tienen cierta capacidad de amortiguación inherente capaz de neutralizar los pequeños cambios en el pH. Sin embargo, puede ser necesario añadir cal si la capacidad de amortiguación no es suficiente.

- El contenido de humedad es el parámetro de funcionamiento más crítico para el buen funcionamiento de un biofiltro (Bagherpour et al., 2005; Tyson et al., 2008). Es por esta razón que se hace necesario un pretratamiento de las corrientes gaseosas a tratar para evitar el secado del lecho filtrante del biofiltro (Figura 1.11). Una baja humedad provocará la disminución de la actividad de los microorganismos, y tal vez la transferencia de los contaminantes adsorbidos por el biofiltro, esto último dependiendo de la naturaleza de los compuestos orgánicos volátiles que conforman el material. El exceso en el contenido de humedad puede causar problemas operacionales disminuyendo la eficiencia de remoción de sistema debido a la aparición de zonas anaeróbicas. La humedad óptima para la mayoría de VOCs estudiados está fijada en el rango entre 50- 60% (Klapková et al., 2006).

- El tiempo de residencia de gas (EBRT), es el tiempo que el gas realmente está en contacto con el material de filtro biológico, y es el tiempo disponible que los procesos de adsorción – oxidación ocurran. El tiempo de residencia variará en función del tipo de olor, teniendo en cuenta que la vida media de estos contaminantes puede ser minutos o días. En general, los compuestos alifáticos se degradan más rápido que los compuestos aromáticos. Los tiempos de residencia recomendados están en el rango de 30 s a 1 min (Stoffella & Kahn, 2005).

- El volumen de los poros debe ser mayor del 80%. Evitando de esta forma posibles zonas anaeróbicas y compactación del lecho que pueden derivar en obstrucciones del biofiltro (Yang et al., 2009).
- La caída de presión a través del lecho del filtro depende de la porosidad, contenido de humedad y compactación del medio. En un biofiltro, la síntesis de biomasa hace que durante el tiempo de operación del mismo se acumule masa microbiana sobre el material filtrante, lo que ocasiona un incremento de la resistencia al flujo que se traduce en una caída de presión (Datta & Grant-Allen, 2005).
- La altura típica del volumen activo de filtración debe oscilar en un intervalo entre 0,5 a 2,0 m, siendo 1 m de profundidad el típico de un biofiltro. Esta área es suficiente para garantizar un tiempo de residencia correcto y minimizar los requerimientos de espacio (Datta & Grant-Allen, 2005; Detchanamurthy & Gostomski, 2012).
- El contenido de nutrientes de los materiales utilizados como lecho en el biofiltro son un parámetro importante a tener en cuenta en el diseño y monitorización de un biofiltro ya que son los responsables del desarrollo de la población microbiana en el mismo. Las fuentes de carbono y nitrógeno para los microorganismos deben provenir del gas contaminante, mientras que otros nutrientes como fósforo, nitrógeno,

minerales y elementos traza deben estar disponibles en el material. Concentraciones muy altas de nitrógeno pueden un efecto inhibitorio en la tasa de remoción del contaminante (Lauderdale et al., 2012)

La puesta en marcha de un biofiltro requiere un tiempo de aclimatación de los microorganismos (Van Groenestijn & Liu, 2002). Los microorganismos generalmente presentes incluyen a hongos, bacterias y actinomicetos. Para las sustancias fácilmente degradables, este período de aclimatación es normalmente de alrededor de 10 días (Bagherpour et al., 2005). Este proceso también permite que los microorganismos desarrollen tolerancias o aceptación a compuestos que pueden ser normalmente tóxicos y que se convierten en fuente de carbono en el nuevo sistema

Las principales ventajas de los biofiltros son: Costos de instalación y de operación son bajos, larga vida útil, condiciones ambientalmente adecuadas, alta capacidad de degradación (98 a 99% para los compuestos típicos del compostaje y para COV en general, 65 a 99%).

Dentro de las principales limitaciones que tiene el proceso de biofiltración se encuentra su operación en abierto, la cual está limitada a factores ambientales.

En la Tabla 1.3 se enuncian las principales ventajas y desventajas del proceso de biofiltración (Mudliar et al., 2010).

Tabla 1.3. Ventajas y Desventajas del proceso de biofiltración.

VENTAJAS	DESVENTAJAS
Costos energéticos de operación bajos	Dificultad para controlar crecimiento de biomasa microbiana
Excepto de sustancias peligrosas en su operación	Eficiencia limitada para concentraciones altas de contaminantes
El contaminante es destruido	Información limitada de diseño y variables de operación
El CO2 producido asociado a esta tecnología es mucho menor	Inestabilidad debido a que es un medio vivo
Diseño simple sin recirculación de agua	Canalización de flujo

Un esquema general de un Biofiltro se observa en la figura 1.11 (Revah & Morgan-Sagastume, 2005).

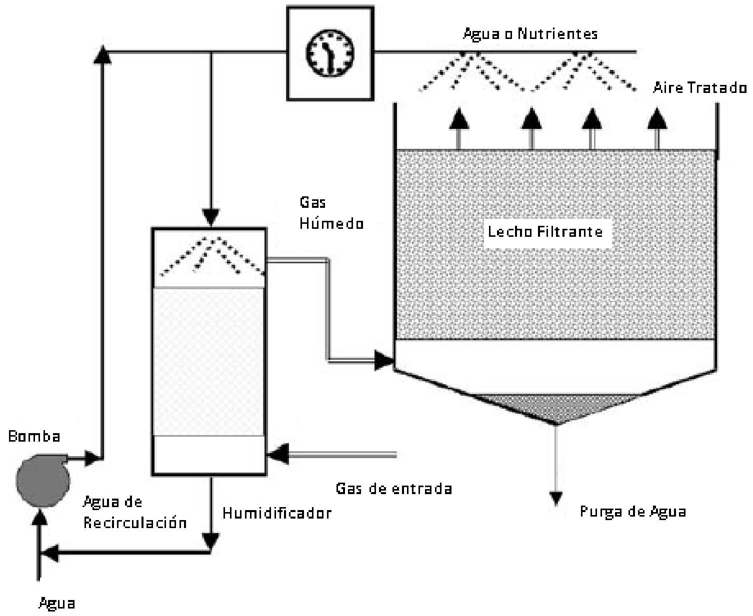

Figura 1.11. Diagrama Esquemático de un Biofiltro Abierto

1.6. MÉTODOS DE CARACTERIZACIÓN DE COMPUESTOS ORGÁNICOS VOLÁTILES (COVs) y OLORES

Teniendo en cuenta que el olor puede ser definido como un estímulo de las células olfativas ante la presencia de compuestos específicos incluyendo COVs y CIVs, existen diversos métodos de medida de los compuestos orgánicos e inorgánicos que causan olor. Tradicionalmente los métodos empleados en la monitorización y caracterización de los procesos que involucran generación y mitigación de COVs y olores se dividen en olfatometricos y procesos físico-químicos (Bidlingmaier & Müsken, 2007).

1.6.1. CROMATOGRAFÍA DE GASES.

El método más fiable para la medición cuantitativa y cualitativa de dichos compuestos (COVs) es la cromatografía de gases (Muñoz et al., 2010) aunque la presencia de un amplio número de compuestos requiere la combinación de diversas técnicas. Sin embargo, debido a la naturaleza compleja de las muestras, esta técnica presenta diversos problemas tales como (Kim et al., 2006):

- Utilización de técnicas auxiliares que involucren sensibilidades diferentes o ejecutar diluciones previas al análisis, debido a las variaciones de concentración de los distintos componentes individuales.

- El carácter inestable de los compuestos presentes en las muestras gaseosas hace necesaria en muchas ocasiones un muestreo “in situ” y “on line”, con lo que la cromatografía de gases presentaría serios inconvenientes en este caso.

- La posible condensación de la humedad de las muestras gaseosas puede generar errores en la cuantificación final de los compuestos analizados, por lo que se hace necesario una minimización del tiempo entre muestreo y análisis.

- La complejidad instrumental de la cromatografía de gases hace necesario realizar un muestreo utilizando bolsas de materiales normalizados como el tedlar o utilizando fibras adsorbentes.

Por estas razones en el caso de un sistema de biofiltración piloto o una planta de tratamiento de residuos, la monitorización de los compuestos orgánicos e inorgánicos causantes del olor requiere el empleo de técnicas más prácticas aunque pudieran ser de menor selectividad en lo que a la caracterización de compuestos se refiere.

Varias técnicas utilizadas en la monitorización de los olores en la actualidad, vienen siendo empleadas hace varios años en otras áreas. Este es el caso de la Cromatografía de Gases la cual se ha utilizado ampliamente en sistemas en los que es necesario separar mezclas orgánicas complejas, compuestos organometálicos y sistemas bioquímicos y como método para determinar cuantitativamente y cualitativamente los componentes de una muestra. En las industrias la cromatografía de gases se enfoca a evaluar la pureza de los reactantes y a monitorear la secuencia de una reacción determinada (Bidlingmaier & Müsken, 2007).

En el caso de la medida de los compuestos volátiles responsables del olor, la cromatografía de gases se ha empleado en conjunto con diferentes variaciones instrumentales. La técnica individual más efectiva empleada en este tipo de problemas en la industria o a nivel de planta piloto es la GC/MS (cromatografía de gases/espectrometría de masas) ya que permite la identificación y cuantificación de los compuestos causantes del olor y sus productos de transformación con gran sensibilidad, principalmente en el caso de análisis “off-line” (Davoli et al., 2003; Defoer et al., 2002; López et al., 2011; Muñoz et al., 2010). Se han realizado varios intentos por mezclar la cromatografía de gases con técnicas útiles en la evaluación de los olores pero de menor exactitud, estos esfuerzos incluyen la integración de la GC/MS con el análisis olfatométrico permitiendo la determinación de las características del olor de los compuestos separados cromatográficamente (Chen et al., 2008; Sohn et al., 2010).

1.6.2. NARIZ ELECTRÓNICA

Los últimos avances en la tecnología de los olores y el interés por simplificar la monitorización de los mismos, reduciendo el análisis, identificación y cuantificación “off-line”, evitando de esta forma posibles errores durante el muestro como la adsorción y la degradación fotoquímica de los contaminantes presentes en las muestras gaseosas, han llevado a la aparición de las narices electrónicas, las cuales debido a su pequeño tamaño y portabilidad permiten realizar fácilmente medidas “in-situ”.

La nariz electrónica se basa en un mecanismo de detección química y de un sistema de procesado capaces de identificar el perfil o huella de olor imitando el sentido del olfato (Sohn et al., 2008).

Una nariz electrónica consta esencialmente de los siguientes componentes (WinMuster_1.6.2.14, 2010):

- *Dispositivo de muestreo*: Para introducir la muestra se usan diversos dispositivos que bien calientan la muestra (en el caso de componentes con baja presión de vapor) para aumentar la concentración en el gas oloroso, o bien pre-concentran la muestra sobre diferentes soportes absorbentes

(Tenax) para después desorberlos térmicamente. De esta forma se pueden conseguir mejoras en el límite de detección de 10 a 1000 veces. El más utilizado es SHS (static headspace) aunque también pueden utilizarse otras técnicas: P&T (purge and trap), DHS (dynamic headspace), SPME (solid-phase microextraction), SBSE (stir bar sorptive extraction), INDEX (inside needle dynamic extraction) o MIMS (membrane introduction mass spectrometry). La introducción directa de la muestra es recomendable para la monitorización de procesos en tiempo real. Algunos equipos incorporan también dispositivos de dilución automática del gas oloroso para evitar la saturación por sobrecarga de los detectores y aumentar su vida útil. En la Fig. 1.12 se muestra el esquema de una nariz con introducción directa de la muestra y dilución automática de la misma.

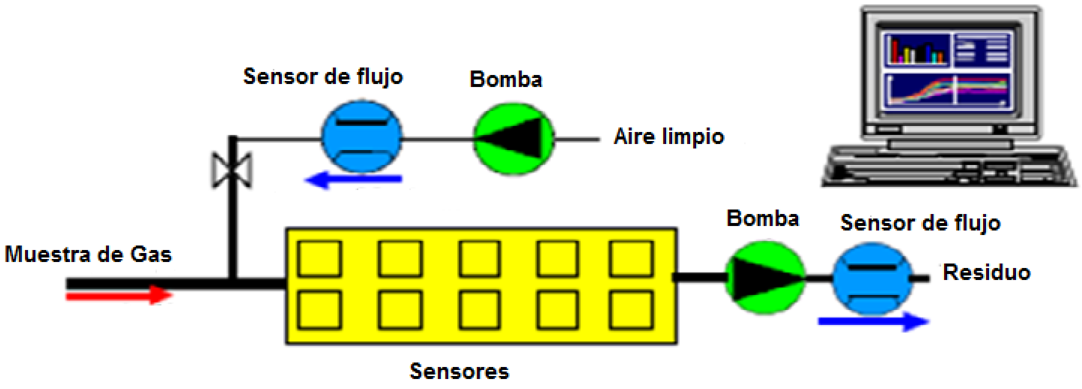

Figura 1.12. Esquema de un sistema de monitorización con nariz electrónica

- *__Sistema de detección:__* El sistema de detección típico de una nariz electrónica es el de un conjunto de sensores de gas (de 5 a más de 20) con especificidad parcial. La selectividad de los diferentes sensores viene determinada por el tipo de material del sensor, el material dopante, la temperatura de trabajo y su geometría. Aunque existen diferentes tipos de sensores los más adecuados para muestras ambientales son los sensores de tipo transistor efecto de campo de metal-óxido (MOSFET) y los de tipo semiconductor metal-óxido (MOS). Como ejemplo, la nariz electrónica PEN3 de Airsense (Figura 1.12) incorpora 10 sensores metal-óxido situados en una pequeña cámara de medida de 1,8 ml. Las últimas tecnologías emplean espectrómetros de masas o espectrometría de movilidad de iones en combinación con el análisis de datos PCA aplicado a los principales picos cromatográficos.

- *Análisis de datos*: La respuesta de una nariz electrónica consiste en el conjunto de medidas de los diferentes sensores. Este conjunto habitualmente se presenta como una "huella de olor". Este conjunto de datos es analizado para reconocer el olor por procedimientos que habitualmente hacen uso del Análisis de Componentes Principales (PCA) (PCA) o bien mediante Redes Neurales. Normalmente este análisis es realizado por un software residente en un ordenador independiente del sistema de detección.

El concepto de nariz electrónica fue introducido originalmente en 1982 en Reino Unido en un intento por realizar una analogía con el olfato humano, reproduciendo la alta sensibilidad del mismo y la alta discriminación entre los compuestos que causan olor. Posteriormente durante el año 1985 en Japón se hicieron valiosos esfuerzos por difundir los resultados experimentales obtenidos en la identificación y cuantificación de olores utilizando un sistema electrónico compuesto por sensores integrados y un microcomputador (Ikegami & Kaneyasu, 1985). Alrededor de 1990 estos prototipos fueron fabricados para su comercialización (Ameer & Adeloju, 2005). En la actualidad existen diversos estudios relacionados con esta clase de dispositivos en el ámbito de la industria alimentaria, más exactamente en el control de calidad de los productos finales y principalmente en la caracterización de los vinos, café y té (Baldwin et al., 2011; Banerjee et al., 2012; Brudzewski et al., 2012; Ghosh et al., 2012; Prieto et al., 2012). Este desarrollo se debe fundamentalmente a sus ventajas prácticas frente a las técnicas cromatográficas de análisis. Sin embargo, deben sumarse esfuerzos para centrar los trabajos futuros en intentar resolver sus principales desventajas como lo son la incapacidad de determinar compuestos químicos específicos en una muestra gaseosa y su cuantificación en términos de unidades de olor. Por otra parte, existen relativamente pocos trabajos relacionados con el uso de la nariz electrónica en la monitorización de procesos generadores de olores como lo son las plantas de tratamiento de residuos sólidos, plantas de compostaje y de tratamiento de aguas residuales, criaderos de animales, estaciones de gasificación (Delgado-Rodríguez et al., 2012; Nicolas et al., 2006; Romain et al., 2005; Sironi et al., 2007; Sohn et al., 2008; Sohn et al., 2009). A su vez, el uso de esta tecnología como herramienta de evaluación de los parámetros de eficiencia en la biofiltración tiene gran potencial, pero es necesario fomentar su uso en base a resultados coherentes a escala de laboratorio y optimizar el tratamiento de los datos generados por la nariz electrónica, con el fin de realizar un escalamiento adecuado de su uso en la industria y en las fuentes generadoras de olores que usen la biofiltración como método de mitigación (Martinelli et al., 2004).

1.6.3. DETECTORES DE IONIZACIÓN

El uso de técnicas como los detectores de ionización, los cuales permiten obtener lecturas en continuo, está bastante extendido en la industria, debido fundamentalmente a su sencillez de manejo, portabilidad, a que la humedad no interfiere en la respuesta obtenida por el detector y a su rápida lectura (<2 s) (Hobbs et al., 1995; Karlik et al., 2002; Ojala et al., 2006). La agencia de protección medio ambiental de Estados Unidos recomienda esta técnica como procedimiento de detección para uso en campo (USEPA, 2007). En el caso de la biofiltración, permite obtener medidas de eficiencia de remoción de forma relativamente fácil y sirve de apoyo en el análisis de los datos obtenidos en paralelo con la nariz electrónica por mínimos cuadrados parciales, ayudando a resolver los problemas de cuantificación de la misma (López et al., 2011).

El Instituto de Recursos Naturales y Agrobiología de Sevilla tiene un amplio historial de investigación en el área del compostaje de diversos residuos y en los últimos años ha estado involucrado, en conjunto con la Universidad de Huelva, en proyectos relacionados con la mitigación de la producción de olores en origen mediante la optimización de los parámetros que controlan los procesos de compostaje (Delgado-Rodríguez et al., 2010; Delgado-Rodríguez et al., 2011). Debe tenerse en cuenta que incluso después de la optimización del proceso de compostaje, las emisiones de compuestos volátiles no se pueden eliminar totalmente, por lo que el presente trabajo de investigación se centra fundamentalmente en el estudio de diversos materiales orgánicos como lecho de relleno de un sistema de biofiltración y la evaluación de su eficiencia y los parámetros que influyen directa o indirectamente en la misma, utilizando las diversas técnicas enunciadas anteriormente para su monitorización en continuo.

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2. OBJETIVOS Y PLAN DE TRABAJO

2.1. OBJETIVOS

Los principales objetivos planteados en este trabajo de investigación se enuncian a continuación:

2.1.1. OBJETIVO GENERAL

- Evaluar el proceso de biofiltración empleando diferentes compost de RSU-Poda como lecho filtrante para el tratamiento de compuestos orgánicos volátiles (COVs) generados en el compostaje de RSU mediante diversas técnicas de monitorización.

2.1.2. OBJETIVOS ESPECÍFICOS

- Estudiar la influencia de diferentes parámetros del co-compostaje de RSU-Restos de Poda (aireación, humedad, relación C/N y tiempo) en los parámetros de estabilidad del compost a través de ensayos controlados, con el fin de utilizar los productos finales más idóneos como material filtrante en sistemas de biofiltración.

- Monitorear las emisiones gaseosas de compuestos volátiles generadas en las diversas fases de un compostaje semiindustrial de la fracción orgánica de residuos sólidos urbanos (FORSU) y restos de jardinería.

- Evaluar el rendimiento de cuatro tipos de compost maduro de RSU-Poda utilizados como lecho en un sistema de biofiltración, con el fin de tratar

COVs producidos durante el compostaje semiindustrial de FORSU y restos de jardinería.

- Determinar el rendimiento de un sistema de biofiltración construido a escala de laboratorio utilizando dos tipos de compost como lecho para tratar corrientes gaseosas contaminadas con Metil Etil Cetona (MEK) y α- pineno en experimentos individuales controlados.
- Analizar la influencia del contenido de humedad de los materiales utilizados como lecho en un sistema de biofiltración a escala de laboratorio en la eficiencia de remoción de corrientes gaseosas contaminadas con COVs hidrofílicos (MEK) e hidrofóbicos (α-pineno) mediante experiencias separadas.
- Estudiar el potencial del uso de la nariz electrónica, el detector de fotoionización de COVs y la Cromatografía de Gases en conjunto con Espectrometría de Masas como técnicas de monitorización de los procesos de biofiltración y de evaluación de emisiones gaseosas contaminantes en general.

2.2. PLAN DE TRABAJO

Este trabajo de investigación hace parte del proyecto CTM2007- 62117 financiado por la Comisión Interministerial de Ciencia y Tecnología (CYCIT) cuyo objetivo principal es la optimización de los diferentes parámetros que rigen el proceso de compostaje, evaluando la influencia de los mismos sobre el proceso integrado, la producción de olores y compuestos orgánicos volátiles (COVs), con el fin de proponer alternativas para la mitigación de los efectos medioambientales, reducir significativamente los costes de inversión y operación para mejorar sustancialmente la eficacia del proceso a gran escala.

Las diferentes actividades y trabajos realizados en esta tesis doctoral se enfocan fundamentalmente en la evaluación del rendimiento de la tecnología de biofiltración para tratar COVs cuyo origen principal es el proceso de compostaje de RSU. En la construcción del sistema se utilizarán como materiales de relleno compost maduros provenientes de ensayos controlados donde se determinará la influencia de los diversos parámetros operacionales del compostaje en los parámetros de estabilidad con el fin de obtener un compost con las características más idóneas para su propósito. A su vez, en la monitorización de los diferentes sistemas de biofiltración se utilizarán diversas tecnologías empleadas en el monitoreo de gases como lo es la nariz electrónica, la cromatografía de gases – espectrometría de masas y el detector de fotoionización de COVs. Todas las técnicas mencionadas se utilizarán paralelamente durante los experimentos con el fin de obtener información lo más selectiva posible del rendimiento operativo del sistema estudiado. Simultáneamente, se realizará una valoración de las diferentes técnicas utilizadas en la monitorización con el fin de establecer las ventajas y desventajas de cada una en este tipo de sistemas, con el fin de tener esto como criterio de selección en futuros trabajos.

El presente plan de trabajo se divide en las siguientes etapas:

1. *Estudio de la influencia de parámetros del co-compostaje de RSU-Poda en los parámetros de estabilidad del compost mediante ensayos controlados.*

Los Residuos Sólidos Urbanos a emplear en esta etapa se obtendrán en la planta de tratamiento de residuos urbanos de Villarrasa (Huelva). Por su parte, los residuos de poda, se recolectaran en el jardín botánico José Celestino Mutis (Palos de la Frontera, Huelva). A su vez, el experimento de co-compostaje se ejecutará en la planta experimental Jack Rodney Harlan de la Escuela Politécnica Superior “La Rábida” de la Universidad de Huelva.

Los experimentos a mediana escala se desarrollarán utilizando reactores de polietileno de alta densidad, con una capacidad de 200 litros y termostatizados mediante espuma de poliuretano, para mejorar las condiciones del proceso.

Se utilizará un diseño de composición central (Box–Behnken) con 3 factores y tres niveles para estudiar la influencia de las variables independientes (aireación, humedad, relación C/N y tiempo), normalizadas entre -1 y +1, sobre las variables dependientes (materia orgánica, Pérdidas de Nitrogeno, Demanda Química de Oxígeno, contenido de nitratos y coeficiente de biodegradabilidad). La monitorización del proceso incluirá el seguimiento de la temperatura del mismo mediante termopares de sensores en continuo e independientes asociados a un equipo de adquisición de datos. La homogeneización de los materiales a recibir tratamiento aeróbico se garantizará mediante volteos periódicos de los reactores. De la misma forma el flujo de aire en cada uno de los compostadores se mantendrá mediante un sistema de aireación. Dicho sistema consistirá en un anillo perforado de PVC en la base del reactor unido a un compresor de aire.

Para la evaluación del proceso de compostaje se realizarán diferentes análisis fisico-químicos mediante el empleo de métodos específicos según normas

UNE. Estos análisis se efectuarán tanto a las materias primas como a los diferentes muestreos durante la ejecución del experimento. Entre los análisis más importantes realizados se encuentran:

Secado y determinación de la humedad de muestras, separación y determinación de impurezas en muestras secas el cual incluye la determinación de la granulometría de las mismas, Molienda de muestras, determinación del contenido en cenizas (Materia Orgánica), Determinación de N - Kjeldahl, composición química (macro y microelementos) mediante plasma (ICP-OES),DQO, pH y conductividad de la fracción orgánica soluble de enmiendas.

La evolución del conjunto de estos parámetros informará sobre el desarrollo y eficacia del proceso y particularmente sobre la biodegradabilidad del material de partida y la estabilidad del producto final bajo la influencia de las distintas condiciones de operación. Esta evolución se realizará mediante un análisis minucioso de modelos polinomiales empíricos de segundo orden para cada uno de los parámetros de estabilidad obtenidos en base al diseño experimental propuesto.

2. *Evaluación del rendimiento de un sistema de biofiltración basado en compost maduros de RSU-Poda para tratar COVs provenientes de una planta piloto semiindustrial de compostaje FORSU y restos de jardinería.*

Se realizará un ensayo de compostaje a escala piloto en un compostador rotatorio (BIOCOMP 3, Kollvik Recycling S.L., San Sebastián, España) ubicado en el campus de “La Rábida” de la Universidad de Huelva, España. Las materias primas empleadas en el proceso de compostaje ejecutado en esta planta piloto serán restos orgánicos de comida y cocina (FORSU) procedentes del comedor universitario de la Universidad de Huelva, separados selectivamente y restos astillados (< 10 cm) de poda de jardinería urbana de Sevilla. Se llevará un control de la cantidad de material adicionado y una caracterización fisicoquímica en diferentes puntos del proceso.

A su vez, se asociará al sistema una batería de 12 biofiltros que recibirá el flujo en paralelo de aire en dos series provenientes del compostador piloto. Los biofiltros se rellenarán con compost maduro de RSU y RSU:Poda (1:1) proveniente de los ensayos controlados de la etapa anterior. Se obtendrán 4 tipos diferentes de materiales filtrantes con 3 triplicados de cada uno, basados en el tamaño de partícula de los materiales (2 a 7 mm y 7 a 20 mm). El diámetro externo de cada biofiltro se fijará en 11 cm y 1 m de altura, a su vez, cada uno presentará un reservorio de agua en la parte inferior de la entrada del flujo (flujo ascendente) con el fin de evitar la pérdida de humedad del gas a tratar. La EBRT se fijará en 44 s.

La monitorización del tratamiento biológico de los gases provenientes del proceso de compostaje se realizará con una nariz electrónica comercial (PEN3, Airsense), un detector de Compuestos orgánicos volátiles con PID (ppbRAE3000 y MultiRAE, RAE Systems, San José, CA, EEUU) y GC/MS (HP 6890 -Agilent Technologies). Utilizando las técnicas mencionadas, se evaluará el rendimiento de cada tipo de biofiltro observando si existen diferencias entre los mismos en función de la eficiencia de remoción, problemas de operación y señal emitida. Esta evaluación se llevará a cabo con la ayuda de técnicas estadísticas de análisis multivariante como el ACP (análisis de componentes principales).

3. *Evaluación del rendimiento de un sistema de biofiltración en laboratorio para el tratamiento de gases con diferentes concentraciones de contaminantes orgánicos volátiles.*

Se construirá un sistema de biofiltración compuesto de un par de biofiltros, utilizando dos tipos diferentes de material filtrante. Los materiales a emplear en esta etapa serán los que presenten menores problemas operacionales y tengan las máximas eficiencias de remoción en la experiencia piloto. Las dimensiones de cada biofiltros serán exactamente iguales a las utilizadas en la anterior etapa.

El aire contaminado a tratar se preparará artificialmente utilizando un burbujeador que contendrá el contaminante en cuestión y permitía ajustar la concentración de entrada al sistema. A su vez, el área de pre-tratamiento del gas a tratar, contendrá un humidificador para garantizar las condiciones de humedad relativa de la corriente gaseosa recomendada en previos trabajos. Los contaminantes utilizados serán los COVs con presencia mayoritaria durante el compostaje a escala piloto y su naturaleza estará relacionada con los dos tipos de biofiltros escogidos. Las concentraciones de los contaminantes se aumentarán paulatinamente con el fin de encontrar la capacidad máxima de remoción de los biofiltros propuestos y evaluar su capacidad de adaptación a cargas intermitentes con diferentes concentraciones de contaminante en los gases de entrada al sistema. La EBRT se fijará en torno a 66 s y el contenido de humedad del lecho se escogerá en base a los resultados obtenidos en la anterior etapa.

Posteriormente se analizará la influencia del contenido de humedad del lecho en la eficiencia de remoción de cada uno de los contaminantes objetos de este estudio. Para esta parte del ensayo, se reducirá inicialmente la humedad de los biofiltros manteniendo constante la concentración de contaminante hasta alcanzar los mínimos de eficiencia. Posteriormente, se restaurará el contenido de humedad de los lechos filtrantes para observar la capacidad de recuperación en el tratamiento de dos compuestos orgánicos volátiles específicos.

Durante esta etapa se realizarán diferentes análisis físico-químicos de las materias primas y de los biofiltros en diversos puntos temporales de la experiencia (cenizas, materia orgánica, nutrientes disponibles, pH, N-Kjeldahl, etc). A su vez, se monitorearán los parámetros fijos del sistema (EBRT, humedad, humedad relativa de la corriente contaminada) con el fin de obtener resultados reproducibles.

La monitorización de esta etapa del trabajo de investigación se realizará utilizando las herramientas mencionadas anteriormente y también se utilizarán métodos de análisis multivariante con el fin de obtener conclusiones concretas acerca del rendimiento del sistema propuesto y por qué parámetros del proceso está afectado durante la degradación de los COVs estudiados.

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3. MAXIMISING MUNICIPAL SOLID WASTE – LEGUME TRIMMING RESIDUE MIXTURE DEGRADATION IN COMPOSTING BY CONTROL PARAMETERS OPTIMIZATION.

3.1. INTRODUCTION

MSW represents an important percentage in waste generation specifically in developed countries. In Europe (EU-27), total municipal waste generation has increased from 239.5 million tonnes to 260.7 million tonnes in ten years, which is equivalent to 524 kg per year per capita in 2008 (European-Commission, 2010). In the case of Spain, 26.3 million tons of municipal solid wastes were collected during 2008, equivalent to 465 kg per person per year (INE, 2010). These volumes highlight the importance of appropriate management of MSW in the country. The best way to reduce the real impact of MSW and of the residues in general, is to minimize its production at source. Nevertheless, despite all the efforts to do this, it is not possible to achieve this completely. Thus it is necessary to find alternatives for the management of the waste, especially for the treatment of the residues enriched in putrescible materials after the removal of dry recyclables and those with a high content of organic fraction. Biological treatments are the most environmental acceptable to treat putrescible residues (aerobic composting or anaerobic digestion). Previous studies confirm that both technologies can maximize recycling and recovery of waste components (Gómez et al., 2006; Mata-Alvarez et al., 2000; Pahl et al., 2008; Walker et al., 2009). Some studies prove that source segregation of MSW followed by recycling (for paper, metals, textiles and plastics) and composting /anaerobic digestion (for putrescible wastes) produces the lowest net flux of greenhouse gases, compared to other options for the treatment of bulk MSW (Eurostat, 2001). Composting is considered both as a waste management method and a process for manufacturing a product at the same time. It can generate income streams in the beginning (disposal costs) and at the end of the process (product sales). There are also important results related to the final uses of the composting product; the compost is increasingly used because of its nutrient value, its ability to rebuild soil organic matter, and also for its capacity to suppress plant diseases (Murillo et al., 1997; Ostos et al., 2008; Stoffella and Kahn, 2005). An additional use of composting products is its use as a bed media in biofiltration systems to treat volatile compounds which are the main source of odours in industry (Dorado et al., 2010; López et al., 2011; Morgan-Sagastume and Noyola, 2006). This alternative is significant because the final product can be used as part of its own production process, (Schlegelmilch et al., 2005). It is important to note that, during 2009, composting represented 18% of waste treatment in Europe (EU27). In Spain, during that same year, around 24% of municipal waste was treated by composting, and this percentage has been increasing during the last few years (Eurostat, 2011). The main factors in the control of composting include: (i) environmental parameters (temperature, moisture content, pH, aeration) and (ii) substrate nature parameters (C/N ratio, particle size and nutrient content) (Bueno et al., 2008). Among the composting process operating parameters studied by several authors, those that demonstrate more influence on composting process or compost quality are: operation time, aeration, moisture and C/N ratio (Bueno et al., 2009b; Delgado-Rodríguez et al., 2010; Habart et al., 2010; Jiang et al., 2011; Madejón et al., 2002).. Porosity and free air space (FAS) are two additional factors to bear in mind because the convenient aeration of the process is only guaranteed with sufficient porosity and FAS. For this reason, the addition of a bulking agent is recommended. The bulking agent reduces compaction, permits gas exchange, makes it possible to adjust the initial C/N ratio, reduces NH_3 emissions and regulates the water content of the composted waste (Chang and Chen, 2010; Doublet et al., 2011; Gea et al., 2007). Wood chips, wood shavings and other lignocellulosic residues are the most widely used materials as bulking agents in composting, representing an additional valorisation of this kind of materials through the process (Adhikari et al., 2009; Delgado-Rodríguez et al., 2010; Eftoda and McCartney, 2004; Yañez et al., 2009).Mathematical composting models are useful for the optimization of the composting process in order to minimize some of its problems (Bueno et al., 2009b; Delgado-Rodríguez et al., 2010; Körner et al., 2003; Madejón et al., 2002; Zhang et al., 2011). Nevertheless few models have been found which study the influence of the many variables simultaneously. These models are created to understand the multiple and complex physical, chemical, biochemical and biological mechanisms that interact in the composting in order to carry out the optimization of the process to obtain an stable product (Illa and Sole-Mauri, 2008). There are two kind of approaches to the models in composting, mechanistic or inductive (which includes the balances of the considered processes) and empiric or inductive (which is an adjustment of the experimental data to equations that describes the processes). Among the limitations of the inductive models are the numbers of unmeasurable factors affecting the process and the great number of experiments to characterise correctly the system (Sole-Mauri and Diaz, 2007). In that case, the experimental design has an important role in the construction of models in order to create the correct number of replicates to extract conclusions about the process parameters and their influence in the final product.

Box and Behnken (1960) introduced an experimental design for three level factors that are widely used to fit second-order models to the response allowing the reduction of replicates in the experiment with the advantage to obtain the same information than traditional designs. Box-Behnken designs were developed by the combination of two level factorial and incomplete block designs. Among the advantages of Box-Behnken designs is the fact that they are spherical and require factors to be run at only three levels. The designs are also rotatable or nearly rotatable and also provide orthogonal blocking. Thus, if there is a need to separate runs into blocks, the designs allow blocks to be used in such a way that the estimation of the regression parameters for the factor effects are not affected by the blocks..

This study aimed to create a model that permits the observation and study of the variables and parameters in the composting process and their interaction, in order to find the best values for these and finally, after future scaling, to apply the model in pilot and large-scale systems. Improved degradation, under low cost technologies, can improve the quality and the cost competitiveness of compost utilization. For this purpose, different properties of solid residues during composting were evaluated.

3.2. MATERIALS AND METHODS

3.2.1. COMPOSTING MATERIALS

The materials used to carry out the composting process were: MSW and LTR. Some relevant characteristics of MSW and LTR are given in Table 3.1.

Table 3.1. Relevant characteristics of Municipal Solid Waste (over dry basis) used in this study (average ± standard deviation [a]).

		MSW[b]	*LTR*[b]
pH (1:5 extract)		5.9 ± 0.2	6.9 ± 0.1
EC (1:5 extract)	dS m-1	8.3 ± 0.1	2.1 ± 0.1
Organic Matter	g kg-1	690.6 ± 8.3	790.3 ± 5.6
Kjeldahl-N2	g kg-1	21.3 ± 1.0	3.2 ± 0.2
C/N		17.1 ± 3.1	128.4 ± 10.8
Bulk density	g L-1	290.6 ± 33.5	92.4 ± 13.2
Particle size			
>25 mm	%	47.5 ± 6.0	--
25-10 mm	%	28.4 ± 2.9	--
10-5 mm	%	13.1 ± 2.2	--
5-2 mm	%	7.0 ± 0.8	--
<2 mm	%	3.9 ± 0.1	--
Impurities >2 mm	%	31.6 ± 3.6	--

[a] Average ± standard deviation, over three samples, (d.w.)

[b] MSW: Municipal solid waste; LTR: Legume Trimming Residues

Municipal Solid Waste was collected in the MSW treatment facility located in Villarrasa (Huelva, Spain). The management activities of MSW performed in this facility are focused on the recovery, preparation and cleaning of recoverable by-products and the use of organic waste by composting treatment. The pre-treatment of the materials prior to composting includes a manual separation of recovery materials (scrap) and undesirable materials (rejects), a screening (8 cm) through a bag-opener trommel and magnetic separation of ferrous materials.

LTR were collected in Campus La Rábida (Huelva University, Palos de la Frontera, Spain), chipped to 2-3 cm and mixed to obtain uniform feed material.

The C/N ratio of the raw materials was adjusted by mixing three different MSW: LTR mass ratio: 1:0, 1:1 and 1:2. Three levels of moisture were obtained (40, 55 or 70%) and fixed before the experimental procedure.

The materials were mixed carefully due to their heterogeneity. Each mixture obtained with the characteristics of the experimental design, was transferred to the composting reactor. Each one was half filled (to guarantee air flow and aerobic conditions) with 40 kg of the mixture of MSW: LTR.

3.2.2. EXPERIMENTAL DESIGN FOR THE COMPOSTING PROCESS OPTIMIZATION.

In order to have different conditions during the composting, a three level, three-factor factorial experimental design was used (Box-Behnken design) (Akhnazarova and Kafarov, 1982). This design allows a designer to adequately quantify a response with a reasonable number of tests. In this sense, Box-Behnken designs require three levels for each factor thus allowing us to evaluate second order models. In this case, the replicated points (with except to center point) can be eliminated from these designs due the high balance and symmetry. For this reason, central composite designs are larger than Box-Behnken designs and provide more degrees of freedom for error estimation.

In order to be able to relate the dependent and independent variables to the minimum possible number of experiments, a orthogonal main effect design consisted of a central one point (central experiment, in the centre of a cube, duplicated) and 16 additional points (additional experiments lying at the cube vertices), was used. All of them were evaluated at three levels, low (denoted as -1) centre point or medium (denoted as 0) and high level (denoted as +1).

3.2.3. STATISTICAL ANALYSIS

The experimental design described above enabled the construction of second-order polynomials in the independent variables and the identification of statistical significance in the variables (Akhnazarova and Kafarov, 1982). The polynomial model used was of the following type:

$$Z = a_0 + \sum_{i=1}^{n} b_i X_{ni} + \sum_{i=1;\, j=1}^{n} d_{ij} X_{ni} X_{nj} \quad (\mathrm{i} < \mathrm{j})$$ (Equation 3.1.)

Where Z and X_{ni} denote dependent and normalized independent variables, respectively, a_0 is a constant and b_i, c_i, d_{ij} are the regression coefficients obtained from experimental data. Independent variables were normalized (X_n) by using the following equation:

$$X_n = \frac{(X - X_{mean})}{((X_{\max} - X_{\min})/2)}$$ (Equation 3.2.)

Where X is the absolute value of the independent variable concerned, X_{mean} is the average value of the variable and X_{max} and X_{min} are their maximum and minimum values, respectively.

The independent variables used in the equations relating to both types of variables were those having a statistically significant coefficient (viz. those not exceeding a significance level of 0.05 in Student's t-test and having a 95% confidence interval excluding zero).

To obtain such models, the normalized values of independent variables and properties of the compost obtained using the proposed experimental design (Table 3.2) have been correlated. Each value of these properties is an average of three experimental results.

The range of values for each independent variable (C/N, aeration and moisture) used in the proposed experimental design is shown in Table 2. At this point, the C/N ratio (C/N) used assumes that the entire N is biodegradable and it is really based on chemical contents. The properties of composting process selected as dependent variables for each model are Organic Matter (%, OM), Nitrate (mg

kg^{-1}, NI), Chemical Organic Demand (mg_{O2} kg^{-1}, COD), Nitrogen-losses (%, NL) and Biodegradability coefficient (k_m). The properties mentioned above are reported as indicator parameters of compost stability by several authors (Bueno et al., 2009b; Diaz et al., 2002; Haug, 1993; Yañez et al., 2010).

Table 3.2. Experimental domain and Box-Behnken design matrix used in the study[a].

Reactor	MSW:LTR[a] (w:w)ratio	C/N	Aeration L_{air} kg^{-1} min^{-1}	Moisture %	C/N, A, M[b]
1	1:2	77	0.300	70	+1, +1, +1
2	1:0	21	0.300	70	-1, +1, +1
3	1:2	77	0.300	40	+1, +1, -1
4	1:0	21	0.300	40	-1, +1, -1
5	1:2	77	0.050	70	+1,- 1, +1
6	1:0	21	0.050	70	-1, -1, +1
7	1:2	77	0.050	40	+1, -1, -1
8	1:0	21	0.050	40	-1, -1, -1
9	1:1	60	0.300	55	0, +1, 0
10	1:1	60	0. 050	55	0, -1, 0
11	1:1	60	0.175	70	0, 0, +1
12	1:1	60	0.175	40	0, 0, -1
13	1:2	77	0.175	55	+1, 0, 0
14	1:0	21	0.175	55	-1, 0, 0
15	1:1	60	0.175	55	0, 0, 0
16	1:1	60	0.175	55	0, 0, 0

[a] MSW: Municipal solid waste; LTR: Legume Trimming Residues
[b] Normalized values for C/N (C/N), aeration (A) and moisture (M) respectively

A pareto chart was constructed with the purpose to analyse the independent variables which have the greatest cumulative effect in the stability parameters of compost studied (Fig 3.1). This figure shows a plot of each dependent variable (stability parameters of compost) against each independent one constructed by changing all the independent variables (composting process parameters) between the normalized values from –1 to +1 in the models constructed.

Having in mind that the influence of the different independent variables on the dependent variables can vary with each value of the first ones, the average change in the dependent variable will be given by:

$$\frac{\int_{(X_{ni})_{min}}^{(X_{ni})_{max}} \left[Z\left(X_{ni}\right)_{max} - Z\left(X_{ni}\right)_{min} \right] dX_{ni}}{\left[\left(X_{ni}\right)_{max} - \left(X_{ni}\right)_{min} \right]} \quad \text{(Equation 3.3.)}$$

Therefore, the change in the dependent variable with that in the independent variable can be expressed as the difference between [Z(Xni)max]max – Z[(Xni)min]min and the previous expression:

$$DZ_i = \left\{ \left[Z\left(X_{ni}\right)_{max} \right]_{max} - \left[Z\left(X_{ni}\right)_{min} \right]_{min} \right\} - \frac{\int_{(X_{ni})_{min}}^{(X_{ni})_{max}} \left[Z\left(X_{ni}\right)_{max} - Z\left(X_{ni}\right)_{min} \right] dX_{ni}}{\left[\left(X_{ni}\right)_{max} - \left(X_{ni}\right)_{min} \right]}$$

(Equation 3.4.)

The figure shows the relative DZi value for each variable. These values allow one to weight the relative influences, as percentages, of each independent variable on the variation of each dependent variable

3.2.4. COMPOSTING REACTORS

The composting reactors were 200 L capacity acrylic barrels. 40 kg of the raw material were placed in the cylindrical reactor. This equated to 3/4 of the total volume of the reactor. To minimize the conductive heat loss via the reactor wall, they were insulated with polyurethane foam. Compressed air (at different rates according to the experimental design, 0.005-0.3 $l_{air}kg^{-1}min^{-1}$) was introduced into the bottom of each reactor and evenly distributed to the composting mixture through a perforated plate. To maintain initial moisture content, water loss was compensated, every day, by the addition of water during active composting.

Two temperature sensors (K thermocouples, TMC6-HA) were placed at the center and the top of the composting mass. An additional temperature sensor was placed outside the reactors to obtain the environmental temperature (Protimeter-MMS-Plus). Temperatures were recorded every 12 h in each reactor by two data loggers (HOBO, U12-006).

The normalized time -1,-0.7,-0.3, 1 corresponds to days 0,10,24,36 of active composting respectively at which compost samples were taken.

3.2.5. ANALYTICAL METHODS

The feedstocks used in the experiment (MSW and LTR), were obtained immediately before the start phase of the composting process. The MSW particle size distribution was determined by a sieve shaker (CISA MODRP.09 Sieve Shaker) and the impurities (glass, plastics, metals and stones) were hand separated and weighed. In the case of LTR, particle size determination was not possible due to its fibrous character. Compacted Bulk Density was determined according to the CEN EN 13040 standard (EN-13040, 1999). The total organic matter was determined by the weight loss after dry combustion at 540 ºC in a muffle for 4 hours (Heraeus D-6450 Hanau) and organic carbon was estimated multiplying the factor 0.58 by the organic matter results (Haug, 1993). Nitrogen was determined by steam distillation after Kjeldahl digestion using a Tecator Kjeltec System 1002 distilling unit (Bremnen, 1996). In the case of MSW, organic matter and nitrogen determinations were done in the < 5 mm size fraction. All the analyses were carried out in triplicate. Compost samples for the analysis mentioned above were taken at days 0, 10, 24 and 36 from the start of the experiment.

Moisture content in the compost samples was quickly determined by an Infrared Moisture Analyzer (COBOS IB110) to correct moisture loss in the reactors. Initial moisture content was determined by oven drying at 105 ºC. The pH and the electric conductivity were determined in 1:5 (weight) compost: water extracts using a pHmeter (Crison BASIC 20+) and a conductivity cell (Crison MicroCM, 2201) according to TMECC method 04.10-A (Thompson et al., 2003).

The Chemical Oxygen Demand (COD) was measured by a colorimetric method (Spectrophotometer HACH DR/2000) in 1:100 (weight) compost: water extracts, using commercial digestion vials with a range of 500-1500 ppm (HACH) after digestion for two hours to 150 ºC in a COD reactor (HACH, 45600) (Garcia et al., 1991; Zmora-Nahum et al., 2005).

Macro and micro elements were obtained by inductively coupled plasma (ICP) spectrometry following nitric/hydrochloric acid digestion (Barnhisel, 1982). The content of nitrate in the different samples of compost was determined in 1:5 (weight) compost: water extracts using a Bran + Luebbe GmbH AA3 dual channel continuous flow auto analyser (Norderstedt, Germany).

The Kjeldahl-N losses during the process (Equation 3.5.) have been calculated from the initial content of N-Kjeldahl, and the evolution of the organic matter, assuming that the mineral amount in each mixture is constant (Bernal et al., 1998; Bueno et al., 2008).

$N_{Loss} = 100 - 100\frac{X_1 N_2}{X_2 N_1}$ (Equation 3.5.)

Where N_1 and N_2 are the initial and final N-Kjeldahl concentrations and X_1 and X_2 the initial and final ash content respectively.

The degradability coefficient (k_m) for the samples (Equation 3.6.) was obtained, at the same time, from the definition of the conservation of ash principle, assuming that inerts entering the process should equal inerts leaving the process at steady state (Haug, 1993). In this way, k_m was calculated using Equation 2.

$k_m = \frac{(OM_1\% - OM_2\%)100}{OM_1\%(100 - OM_2\%)}$ (Equation 3.6.)

Where $OM_1\%$ is the initial total organic matter content, % of total solids and $OM_2\%$ is the final total organic matter content, % of total solids.

3.3. RESULTS AND DISCUSSION

To gather information on the agronomic value of the raw material, analyses on the nutrient content were performed (Table 3.1). In this sense, results revealed adequate properties for both raw materials to be co-composted. The moderate salinity (EC) of MSW and the high C/N ratio of LTR could be counterbalanced among both residues. The low concentration of heavy metals (data not shown) confirms the safety in term of metals of the original materials.

Substituting the values of the independent variables for each dependent variable in Table 3.2 into the polynomial expression used by the models, yielded the equations showed in Table 3.3.

The differences between the experimental values and those that were estimated using the previous equations never exceeded 10% of the former. The equations obtained have a coefficient of determination (r^2) from 0.81 to 0.95 which suggest that the model is reliable in order to represent the system studied and predict the optimum values of control parameters.

Table 3.3. Equations yielded for each dependent[a] variable as a function of the independent variables[a].

Compounds	r^2 [b]	F[b]	df[b]
OM= 61.88293 - -1.57455 *T -4.26918 * M + 15.18732 *CN -4.96636 * M^2 -4.91715 * CN^2 -3.47587 * M CN	0.89	65.0	6.53
NI= 37.7710 + 86.0151 * T -49.6935 * CN + 57.5314 * T^2 - 72.1740 * T * CN	0.95	300.2	4.55
COD= 10507.5 -18159.2 *T -3933.1 * A -6745.5 * CN +25632.1 * T^2 +8040.0* CN2 +3057.7* T * A +6628.1* T *CN +3921.9 A * CN	0.91	65.6	8.51
NL= -2.48229 -2.68113 *T + 5.00057 * M -4.78448 * T^2 +4.64456 M^2 +4.26726 CN^2 +7.57182 A M	0.81	37.9	6.53
KM= 0.635431 +0.213008 *T +0.043159 *M -0.213974 *CN -0.400391 *T^2 -0.130694 * T *CN +0.041150 *M * CN	0.90	77.0	6.53

[a] r^2, F and df denote coefficient of determination, Fisher-Snedecor distribution and degrees of freedom respectively. The differences between the experimental values and those estimated by using the previous equations never exceeded 10-15% of the former.

Where: T,A, M, CN denote the normalized value of the operation time, aeration, moisture and C/N ratio, respectively as independent variables. In addition, OM= Organic Matter (%). NI= Nitrate (mg kg-1), COD= Chemical Organic Demand (mgO2 kg-1), NL= Nitrogen-losses (%) and KM= Biodegradability coefficient as dependent variables

[b] Each value is the average of three samples, dry weight basis. Percentages with respect to organic matter content.

3.3.1. PARETO CHART ANALYSIS

Moreover, the crossed interactions between two independent variables terms in the equations (Table 3.3) make difficult the identification of the degree of influence of the independent on the dependent variables. Thus, a Pareto chart, also called a Pareto distribution diagram, is used to compare the cumulative effect of each of the independent variables ($p<0.05$). Fig. 3.1 shows a plot of each dependent variable (compost stability parameter) and its Pareto chart of standardized effects (as percentages) based on independent variables.

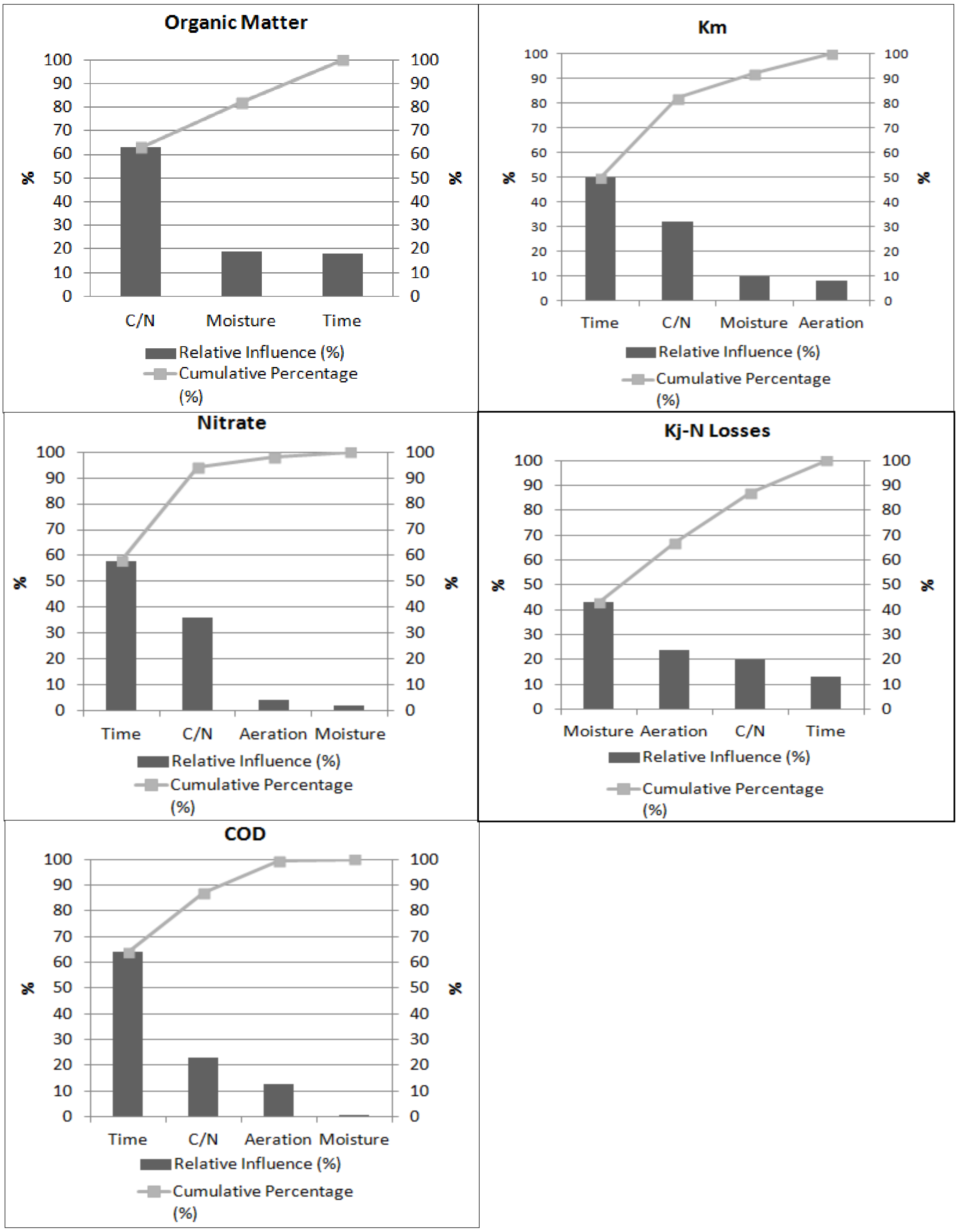

Figure 3.1. Variation of dependent variables as a function of normalized independent variables (Pareto Chart).

As can be seen, the C/N ratio is the strongest variable influencing OM evolution which indicates that the nature of the materials affects its transformation more than the classical variables like moisture or aeration. Moisture has the strongest effect on N-losses; time was found to be the most influential factor on nitrate, COD and biodegradability. Aeration shows a lower effect on the selected composting evolution parameters, which may indicate that even the lower aeration rate selected could maintain aerobic conditions. Moreover, moisture also shows small effect on these parameters with the exception of N-losses which could indicate that the daily moisture adjustments maintained enough water in the system even in the lower level.

3.3.2. ANALYSIS OF COMPOST STABILITY PARAMETERS.

In order to determine the values of the independent variables giving the optimum values of the selected dependent variables, the predicted evolution for each variable was plotted at the three selected levels of the most influential independent variable and for a fixed value of the least influential variable (Figs. 3.2–3.6).

3.3.2.1. Organic Matter

The OM (Fig. 3.2) variation indicates the relative decrease of the content of this parameter during the composting process. As expected, high OM content under high C/N ratio is observed (Yañez et al., 2009).The higher variation of the OM content was observed under greater C/N ratio ; which agrees with the results of previous reported studies. Nevertheless, this evolution basically depends on the raw materials used and its pre-treatment (Bernal et al., 1998; Diaz et al., 2002; Jiang et al., 2011; Nada et al., 2012; Rao et al., 1995). As expected, for all the C/N ratios, the OM losses tended to stabilise at the end of the composting process (Raj and Antil, 2011). In the case of the highest C/N ratio studied, greater carbon content seems to promote OM losses throughout the composting, despite the fact that the most easily biodegradable substances are metabolised during the first stage of the process (Benito et al., 2003). However, a long composting time did not produce low OM values under a high C/N ratio, this effect could be due to less biodegradable carbon sources, like lignocellulosic residues, found in LTR. The used LTR are basically made of cellulose (60.19±3.37% over dry organic matter), hemicelluloses (22.51±1.83%) and lignin (14.10±1.47%). These components account for 92% of the LTR composition, the other percentages correspond to fats, resins, waxes, minerals, etc. Though the percentage of decomposable cellulosic materials, such as cellulose and hemi-cellulose in this residue is high, the lignin fraction could protect them from decomposition. Because lignin is the most recalcitrant component of the plant cell wall, a higher proportion of lignin implies a lower bioavailability of the substrate. The effect of lignin on the bioavailability of other cell wall components is thought to be largely a physical restriction, with lignin molecules reducing the surface area available to enzymatic penetration and activity (Haug, 1993). It is known that lignin can persist for very long periods of time (Tomati et al., 1995; Tuomela et al., 2000; Yañez et al., 2010).

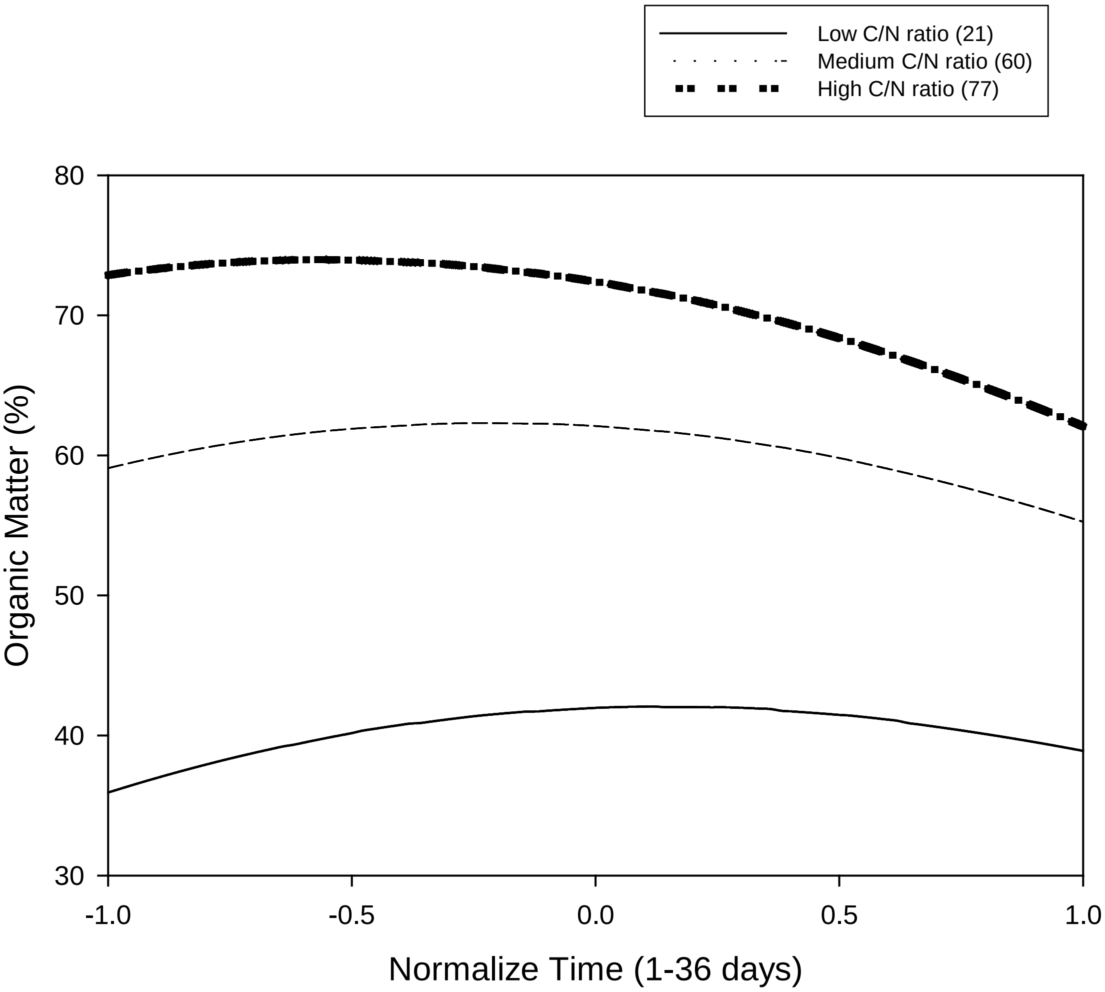

Figure 3.2. Organic Matter evolution as a function of time and at three C/N ratio levels.

3.3.2.2. *Degradability Coefficient (k_m)*

The former explanation is reinforced by the evolution of the predicted biodegradability values (Fig. 3.3) of the composted materials, which also were highly and inversely dependent on C/N ratio (Yañez et al., 2009). Some studies have concluded that lignin content is the predominant factor in determining the extent of substrate degradation (Haug, 1993). Thus, a low C/N in this case, corresponding to a minimum LTR content, is the desirable condition to obtain high biodegradability values. In all cases, the influence of time on this parameter is clear (Fig. 3.1.). In fact, an increase in biodegradability, up to 30 days, has been found. Nevertheless, after that, consequent stabilization has been found in all the studied reactors. It should be noted that, as expected, an inverse relationship between biodegradability and OM evolution was found (Haug, 1993).

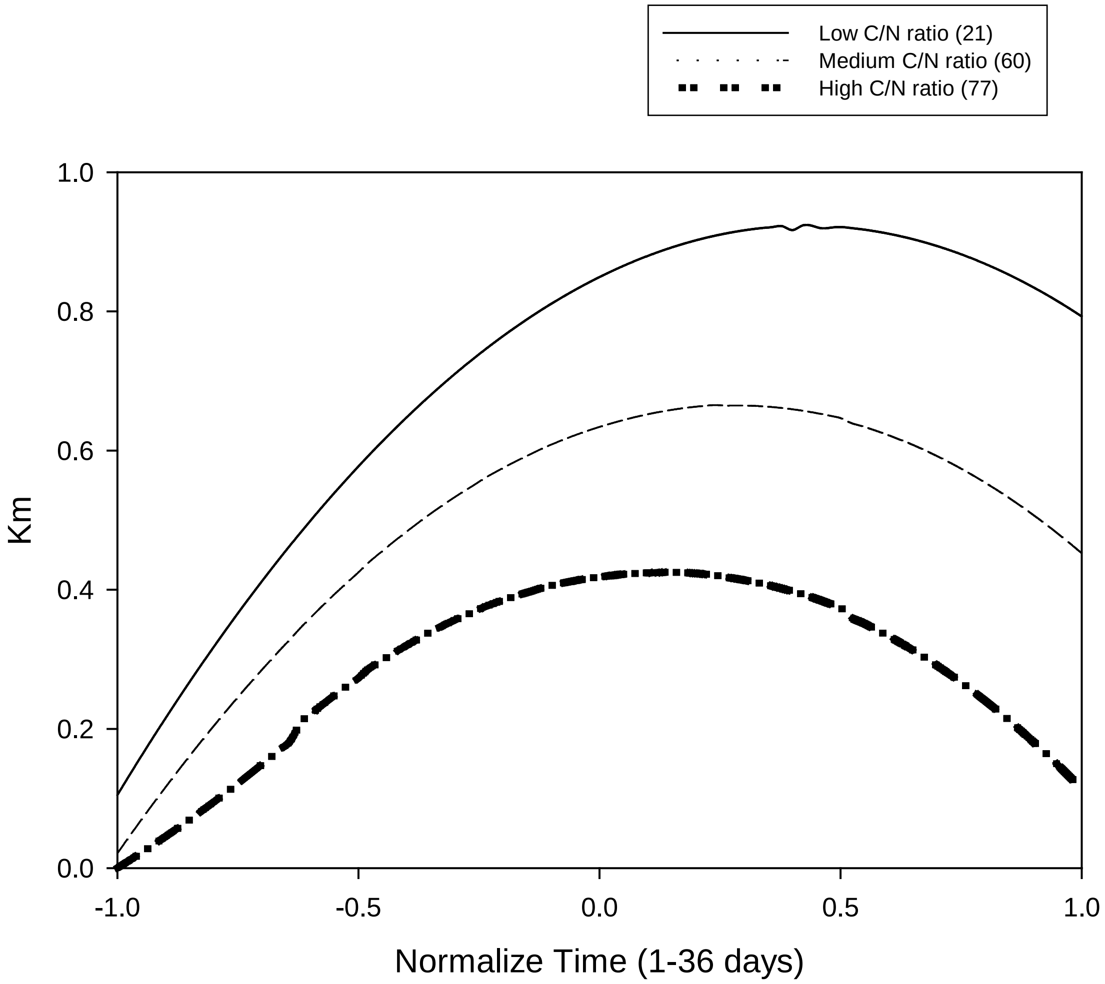

Figure 3.3. Biodegradability coefficient evolution as a function of time at three C/N ratio levels.

3.3.2.3. *Nitrate content*

The NO_3^--N evolution (Fig. 3.4.) was much more sensitive to changes in the C/N ratio than the other variables studied. The greatest changes in NO_3^--N resulted from variation of this parameter (94.6% with respect to the maximum value). NO_3^--N values obviously increased with composting time and lower C/N ratio (Bueno et al., 2009a). The NO_3^--N increase is negligible at a high C/N ratio, being the NO_3^--N values at the end of composting similar to the initial values of this parameter (Bernal et al., 1998; Jiang et al., 2011). Previous studies have reported that aeration significantly influences the nitrification process (Bueno et al., 2009a; Habart et al., 2010). This fact could be explained due to the high influence of aeration in the NH_4^+ to NO_3^- transformation (Haug and Ellsworth, 1991). Nevertheless, in this case aeration seems to be less important than other parameters like C/N ratio and time, which indicates that the aeration rates proposed in the experimental design are enough to guarantee the nitrification process avoiding anaerobic conditions and encouraging the production of stable compost. It is important to notice, that the NO_3^--N content increased in the last stages of the composting, when temperatures lower than 40 ºC do not inhibit the nitrification process (Stoffella and Kahn, 2005).

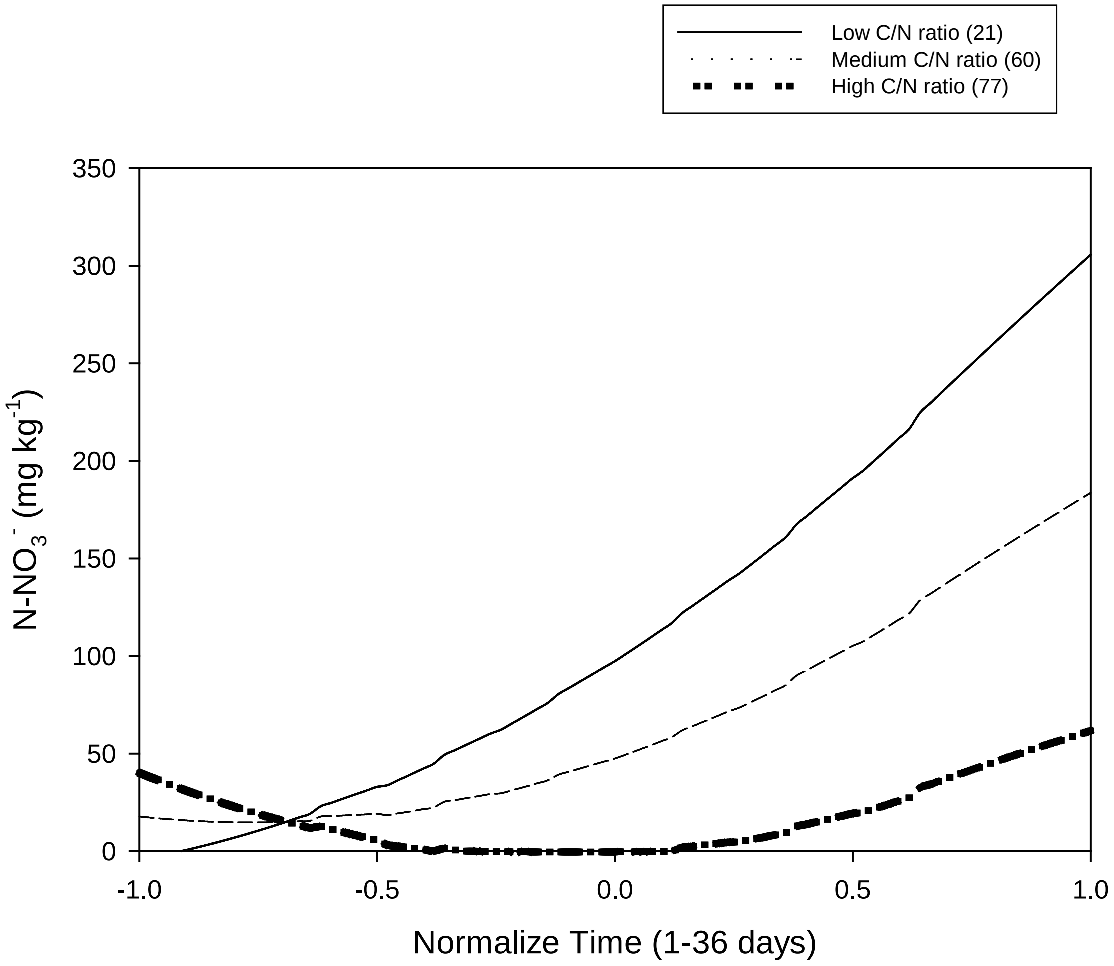

Figure 3.4. N-NO3- variation as a function of time at three C/N ratio levels.

3.3.2.4. N-losses

As can be seen in Fig. 3.5., obtaining maximum N-losses entails using high moisture content. The C/N ratio, in this study, shows a low influence in N-Losses, though was greater than the one found for aeration. As expected, high N-Losses values (12%) are observed during the most active stage of the process (high organic matter degradation). If the primary goal is to minimize N-losses, by exploiting the whole potential of the raw material in its use as fertiliser, low or medium moisture must be used. Spite of the reported N-losses a relative increase of nitrogen (6 %) with respect to its initial content is observed. It could be due to the higher organic matter losses, under medium and low moisture levels, which surpassed the N-losses (Jiang et al., 2011). Moisture is an important parameter in the composting process; low moisture content in the materials reduces microbial activity, whereas high content affects physical properties reducing the free air space, modifying the air diffusion and creating compaction (El Kader et al., 2007). For this reason, it is important to guarantee medium levels of moisture in the materials throughout the composting process. Previous studies in this area prove that minimum N-losses were obtained at moisture content between 40% to 55% (Bueno et al., 2008; Bueno et al., 2009a). The fact that the high moisture levels had a positive effect on the N-losses could be due to the fact that the nitrification, denitrification and N_2 production processes increase as the moisture content increase (Hwang and Hanaki, 2000).

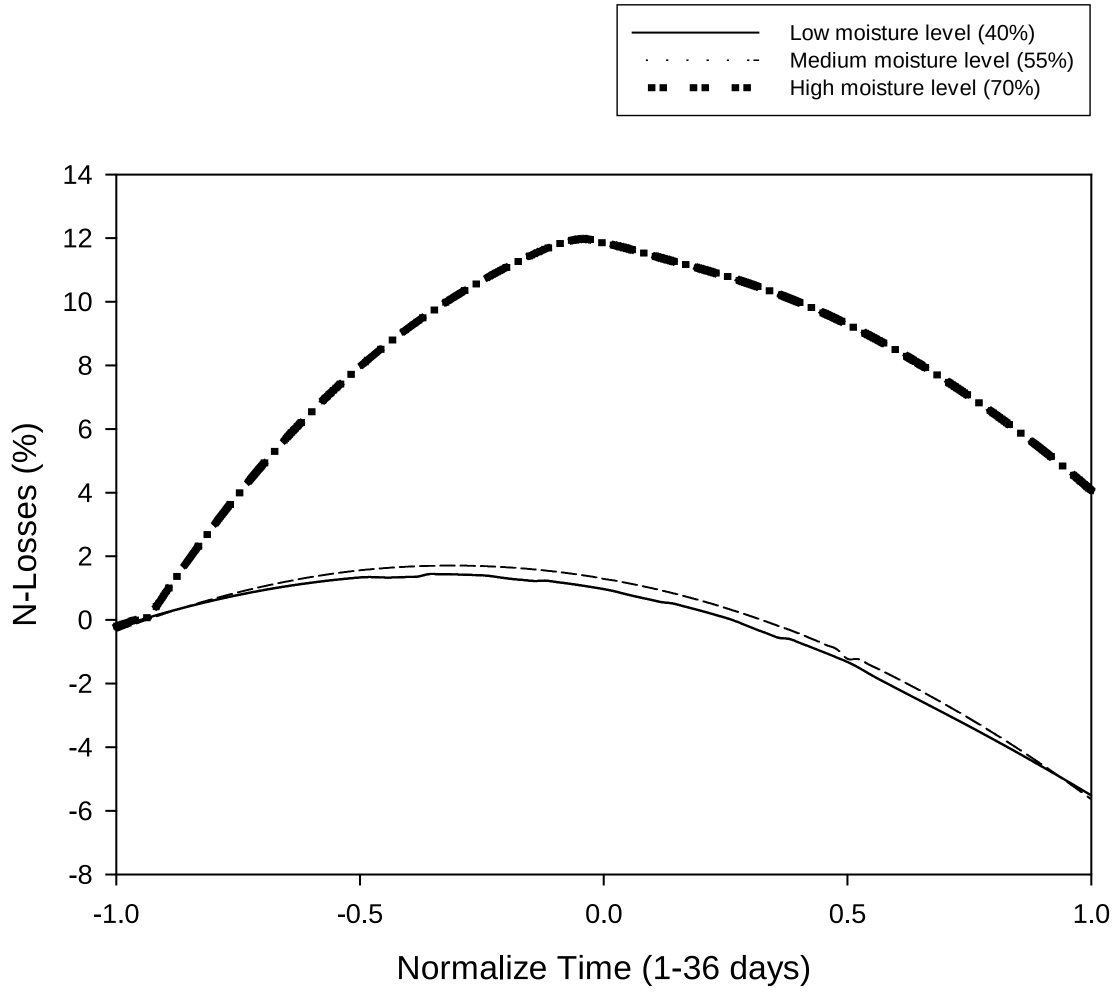

Figure 3.5. N-Losses variation as a function of time at three moisture levels.

3.3.2.5. *Chemical Oxygen Demand (COD)*

The COD (Fig. 3.6.) is a parameter related to compost stability (Haug, 1993) and may indicate the presence either of microbial stabilization, or it may be due to the presence of toxic organics inhibiting the microbial activities. This study showed that the relative decrease of COD was similar under the three C/N conditions, and tended to approach zero at the end of composting. Decreasing of the COD ratio meant that the compost became non-biodegradable, or stable in terms of no further biodegradation (Fdez.-Güelfo et al., 2011; Haug and Ellsworth, 1991). The absolute decrease of COD values was greater under low C/N ratio; this fact could be explained by the higher availability of dissolved carbon present in the MSW compared with the materials with high C/N ratio such as LTR, where the carbon content is linked to the lignin due to the composition of the raw materials used to adjust this ratio. As expected, the same as with the degradability coefficient, time is an important variable influencing this parameter, which indicates that time has an influence on the process to obtain stable compost products. The time profile of compost stability could be divided into 2 stages, i.e. stage 1 (compost age between 0 and 15 days), stage 2 (after 15 days) which were classified as active degradation and the stability period respectively. The compost would be stable after 30 days.

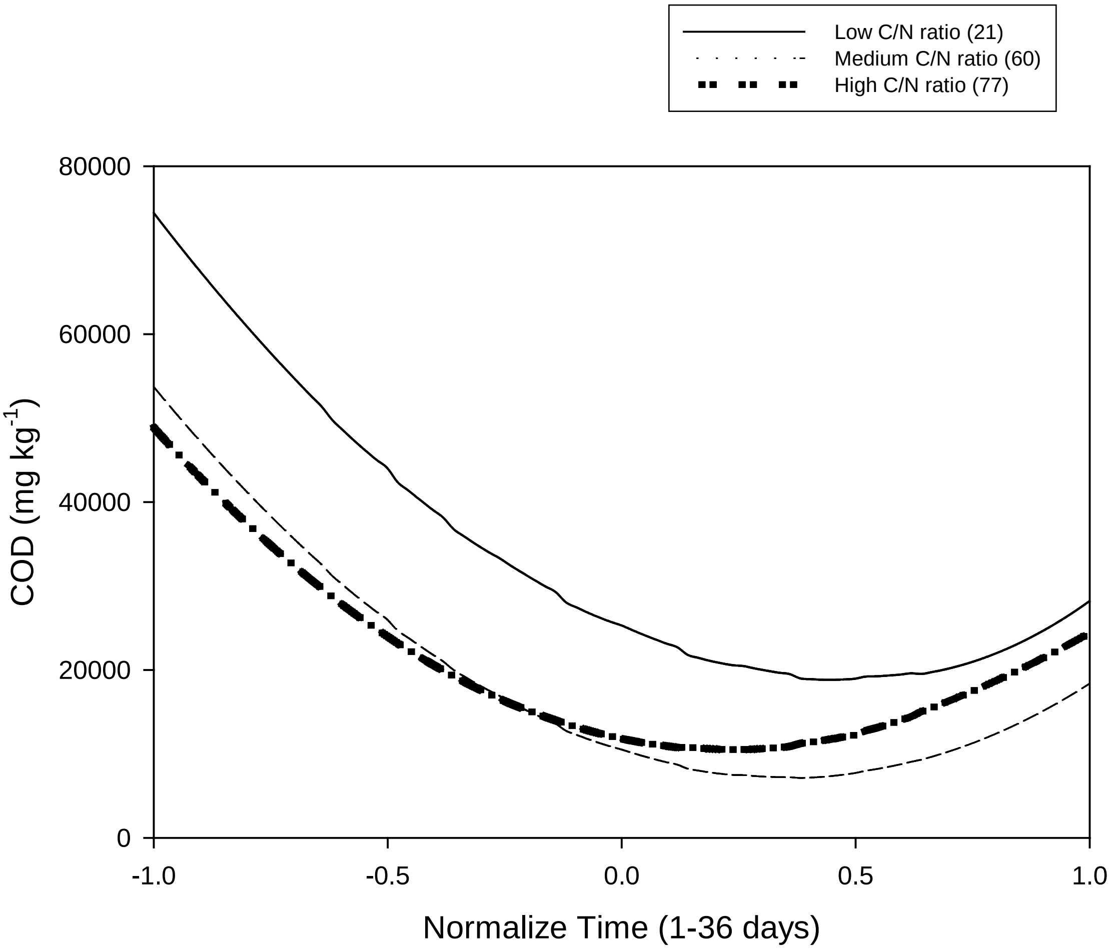

Figure 3.6. COD variation as a function of time at three C/N ratio levels.

3.4. CONCLUSIONS

Both materials (MSW, LTR) evaluated in this study were adequate feedstocks for co-composting.

The C/N ratio is the strongest variable influencing OM evolution. The losses of organic matter were reduced when MSW was co-composted with a minimum of LTR (lower C/N ratio). Nevertheless, the biodegradability and the N-losses increased under these conditions.

On the other hand, moisture has the strongest effect on N-losses. The minimum N-losses during the composting process were found under medium and low values of this parameter (40-55 %).

The weak influence of aeration on the dependent parameters indicates that an air flow of 0.05 L_{air} kg^{-1} min^{-1} is sufficient to guarantee the aerobic process.

Time is an important parameter directly influencing the degradation of the materials during the process and affecting the stability of the products.

The results of the modelling suggest that an optimized ratio MSW/LTR of 1/1 (w/w) (equivalent to C/N 60), moisture content in the range of 40-55% and moderate to low aeration rate (0.05-0.175 L_{air} kg^{-1} min^{-1}) is recommended to maximise degradation and to obtain a stable product during co-composting of the described raw materials.

The predicted evolutions and the relations among independent and dependent parameters obtained from the model used are in concordance with the current knowledge of the composting process, showing this model could be effectively applied to the composting process.

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4. BIOFILTRATION OF COMPOSTING GASES USING DIFFERENT MUNICIPAL SOLID WASTE-PRUNING RESIDUE COMPOSTS: MONITORING BY USING AN ELECTRONIC NOSE.

4.1. INTRODUCTION

Composting facilities are a great source of unpleasant smells, generating a nuisance to nearby residents and causing rejection of these kinds of facilities (Müller et al., 2004; Schlegelmilch et al., 2005; Smet et al., 1999). These smells are caused by substances such as some inorganic gases (ammonia and hydrogen sulphide) and volatile organic compounds (VOCs) released during the biodegradation of organic residues (Müller et al., 2004; Shareefdeen et al., 2005). Generally, the reached concentrations of VOCs and other odorant gases are not of toxicological relevance, but the people working or living in the vicinity of the composting plants may suffer diverse psycho-hygienic effects (Müller et al., 2004). Consequently, several countries have established regulations to guarantee nuisance-free, breathable air. The legislation copes with this problem in two ways: setting minimum distances from the facilities to housing or limiting the odour emissions from them. The abatement of odour and VOC emissions in the facilities could be achieved through an adequate control of the composting conditions. Schelegelmilch et al. (2005) indicated the dependence of odours on some operations (storage, turning, screening, cleaning) carried out in the composting plants. Recently, Delgado-Rodríguez et al. (2010) studied the influence of process parameters (C/N, moisture and aeration) on VOC emissions. Once air streams in a composting plant could be collected, biofiltration is considered as a recommended technology for the final VOCs abatement because of its capacity to treat low concentrations of diverse pollutants, its cost-effectiveness, simple operation and absence of secondary contaminated waste streams (Datta and Allen, 2005; Namkoong et al., 2003; Pagans et al., 2006). Common biofilter media include peat, wood bark, wood chips, soil, compost, coated ceramic particles, synthetic media or a combination of these products (Schelegelmilch et al., 2005; Shareefdeen et al., 2005). Nevertheless, few studies have compared different materials or composts (Álvarez-Hornos et al. 2008).

Several analytical methods, usually in conjunction, have been used for the monitoring of gas concentrations in the composting and biofiltration process. Characterization and determination of specific VOCs are performed by a variety of gas chromatography (GC) instruments, mass spectrometry (MS) and flame ionization detector (FID) being probably the most frequent detection techniques (European Commission, 1999). Wang and Austin (2006) reviewed sampling and analytical methods for VOCs in air and they concluded that current inventories of VOC emissions remain subject to considerable uncertainty due to variation in methods. Several authors (Karlik et al., 2002; Ojala et al., 2006) have suggested the possibility of using total-VOCs analysers equipped with PID detector to obtain rapid information on the concentration of VOCs. The USEPA (2007) recommends this instrument as a screening procedure for field use. Each different VOC produces different signal intensity in the PID detector. In the case of a single VOC gas, the reading of the VOCs analyser can be a reliable measure of its concentration as long as the instrument is calibrated with the same VOC. In the case of gas mixtures differing in composition, the VOCs reading is considered a semiquantitative approach of the total concentration of VOCs, referred to the calibrating compound. In this sense VOCs measurement is similar to odour determination by olfatometry: the obtained value denotes the sum of single VOC signals, each one proportional to a correction factor or threshold. In contrast to odour concentration, readings of the VOC analyser vary linearly with the concentration of VOCs. Additional advantages of the VOCs analyser are its portability, accuracy and quick response time (< 2 s). Chemical (GC-MS) and olfactory analysis have been used serially a few times (Chen et al. 2008). Gas detector tubes for sampling and quantification have also been used for selected compounds or VOCs families (Tsai et al., 2008).To measure odour emission (or concentration) as a whole, olfactometry is generally the selected method (Mao et al., 2006; Tsai et al., 2008). The European Union adopted the standard olfactometric method EN 13725 (CEN, 2003) based on dilution of an odorous sample to the odour threshold detectable to 50 % of a test panel (Schelegelmilch et al., 2005). Even though standardized olfactometric methods permit enough reproducibility and they are reliable for concentrated emissions, their applicability for low concentrations was doubtful (Littarru, 2007). Olfactometry is a time- and cost-intensive method and the applicability of a human panel especially for field measurements involves practical difficulties (Muller et al., 2004; Figueiredo and Stentiford, 2001). Since the eighties, but particularly during the last decade, electronic noses (e-noses) have attracted interest to overcome the limitations of the human sense and have been used for qualitative and quantitative gas analysis in environmental monitoring (Ameer and Adeloju 2005). Although e-noses have been used in composting studies, their application for the comparison and monitoring of biofilters has not been studied widely.

This work studied the reduction in the concentration of VOCs during the biofiltering process of the air from the composting of kitchen waste and pruning residues. Four composts, differing in their originating materials and particle-size, were used as biofilter media. The qualitative changes in the biofiltered air were assessed by an e-nose.

4.2. MATERIALS AND METHODS

4.2.1. COMPOSTING PROCESS

Composting was carried out in a rotary drum composter (BIOCOMP 3, Kollvik Recycling S.L., San Sebastián, Spain). The rotary drum has a capacity of 1800 L and is equipped with automatic heating (not used, maximum temperature reached 47 ºC), ventilation (230 m^3h^{-1}, in 12 periods day^{-1} of 6 min), turning (2 revolutions per day) and mixing systems. The composter was fed 18 times (3-4 days per week) during 5 weeks with variable volumes of kitchen waste (MSW) (45 to 180 L day^{-1}, average 73 L day^{-1}) and shredded pruning waste (P) (23 to 102 L day^{-1}, average 51 L day^{-1}) which corresponds to 1.42:1 kitchen waste:pruning waste volume ratio. The kitchen waste was obtained from the University canteen (La Rábida, Huelva, Spain). It contained source separated food waste from the canteen and the kitchen, including paper mats from the trays. The pruning waste originated from Sevillian gardens and contained a mixture of wood and leaves from several species. The maximum size of wood chips was about 10 cm. Average bulk density of the kitchen waste was 0.228 kg L^{-1} (0.159 - 0.294 kg L^{-1}), and average bulk density of the pruning waste was 0.151 kg L^{-1} (0.079 - 0.288 kg L^{-1}).

4.2.2. BIOFILTRATION UNIT

The air from the composter was extracted by an exhaust fan and was distributed upstream to a set of 12 pilot-scale open-top biofilters (3 blocks with 4 treatments). The distribution line and the biofilters were made of PVC. A sampling port for the inlet gas was situated before the distribution line. Each biofilter consisted of a column of 11 cm diameter and 1.5 m height. The upper part of 95 cm height (bed volume 9.0 L) was filled with compost. The sampling of outlet air was done at the top of each biofilter. The bottom of the biofilter (40 cm height) was filled with water to maintain moisture content in the biofilter bed. The air from the composter was connected just on top of the water level. A schematic diagram of the biofilter unit is shown in figure 4.1.

Four kinds of biofilter media were used: MSW mature compost (MSW2) with particle size ranging from 2 to 7 mm; MSW mature compost (MSW7) with particle size ranging from 7 to 20 mm; MSW and pruning waste (1:1 volume ratio) compost (MSWP2) with particle size ranging from 2 to 7 mm; and MSW-pruning waste compost (MSW7) with particle size ranging from 7 to 20 mm. Pieces of glass and media with particle size less than 2 mm were discarded to avoid biofilter clogging. Additional details about the composting process of these composts can be obtained from Delgado-Rodríguez et al. (2010). The fraction 2-7 mm was similar in size to that recommended (3-8 mm) by Cudmore and Gostomski (2005) as the major mass fraction for graded bark used in biofilters. Moisture contents of biofilter media were adjusted to 40%, 38.23%, 59.80% and 55.36%, for MSW2, MSW7, MSWP2 and MSWP7 respectively. These values were adjusted by adding increasing amounts of water to the biofilter media to the maximum before free water was observed. Initial moisture content was determined by oven drying at 105ºC. During the course of the experiment moisture was maintained in the biofilters by weighing the complete biofilter bed and by adding the lost water to each biofilter to its top. The empty bed residence time (EBRT) was adjusted to 44 s. EBRT values about 1 minute were frequent in biofiltration experiments (Álvarez-Hornos et al. 2008, Pagans et al. 2006).

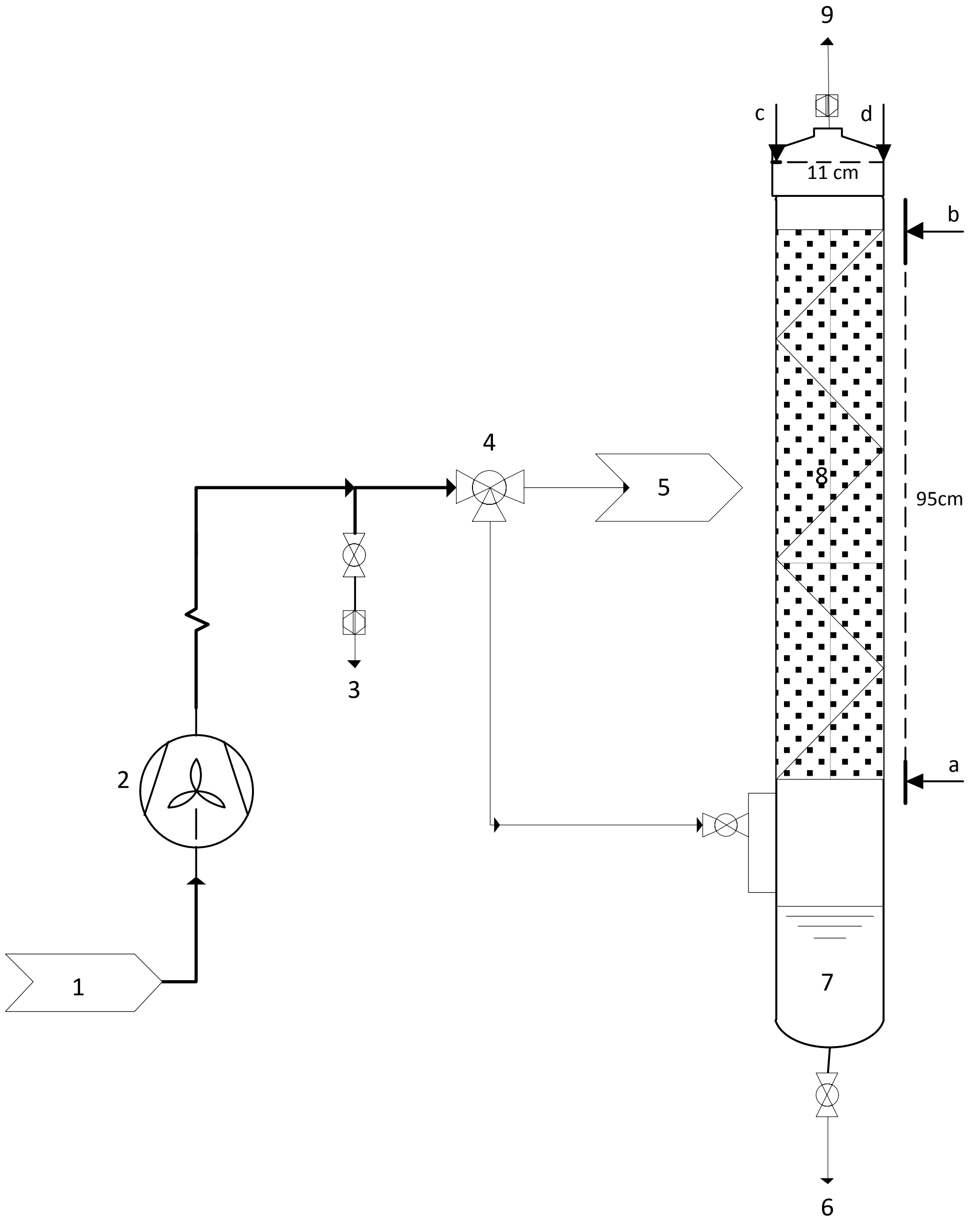

Fig. 4.1. Scheme of the pilot-scale biofiltration system. (1) Composter drum/Exhaust gases from composter and inlet biofilter gas; (2) Fan/Extractor; (3) Input sampling port; (4) Flow splitter; (5) Inlet stream to a 11 (+1) biofilters battery; (6) Water drainage; (7) Air humidification zone; (8) Compost bed; (9) Outlet biofilter gas / Output sampling port.

4.2.3. TOTAL-VOCS ANALYSIS

A portable VOCs analyzer fitted with a 10.6 eV lamp for photoionization (ppbRAE3000, RAE Systems, San José, CA, USA) was used in this work. Air was taken from the lines by means of an internal sampling pump with a flow rate of 0.5 L min^{-1}. The reading was taken when it stabilized, usually in a time less than 30 s. This instrument does not detect water but its condensation on UV lamp could provoke a loss of signal (Ojala et al. 2006). To avoid this effect, sampling lines were kept to a minimum and a Teflon filter (0.45 µm pore size) was used as a water and particulate material trap. The instrument was calibrated with isobutene, and the result, whose unit is ppb_v, refers to the response of the total VOCs as isobutene equivalents.

Removal efficiency of VOCs was calculated as the percentage reduction in VOCs content from output to input biofilter air. The average of three replicate measurements was used for the calculation.

4.2.4. ELECTRONIC NOSE MEASUREMENTS

In this work, PEN3 e-nose (Portable Electronic Nose, Airsense Analytics GmbH, Hagenover, Schwerin, Germany) was used. The e-nose has an array of 10 different metal oxide sensors (MOS) positioned inside a small chamber (1.8 mL). Orzi et al. (2010) described a similar e-nose with the same sensor number and type. The analytical system has a special integrated sampling system, which by an automatic control (autoranging) prevents overloading of the sensors and also leads to better and faster qualitative and quantitative analysis. The time necessary to achieve signal stabilization was about 30 s. A time of 48 s was selected as stabilization time, then sensor readings were taken during 2 sA time of 60 s was used as purging time between consecutive measurements.

4.2.5. AIR SAMPLING

Direct reading was done from the biofilters inlet and outlet ports using the VOCs analyser and e-nose simultaneously while the ventilation fan drove air through the biofilters. At the outlet, a hood was placed on the biofilter top, and the sampling tubes were situated inside the hood. Each reading was done in triplicate in each biofilter, with a 120 s difference between consecutive replicates. Readings of the input air were taken between each block of 4 biofilters. The monitoring of the biofilters was done 0, 1, 5, 6, 12 and 20 days after the first feeding to the composter. The sampling with VOCs analyser was also done continuously during a 24 h period at the inlet and outlet in one of the biofilters.

4.2.6. STATISTICAL ANALYSIS

One-Way ANOVA and Tuckey's HSD test were used for analysis of the variance and comparison of means. Biofilter type was considered as the independent variable and biofilter characteristics or VOCs removal efficiencies as the dependent ones. A p value lesser than 0.05 was selected, The procedures were executed with the statistical software SPSS 15.0 for windows (SPSS Inc).The large data sets from e-nose were elaborated through statistical methods such as principal component analysis (PCA) for data reduction. The data reduction is displayed in a two dimensional figure, 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. Euclid and correlation classification have been used as sample classifiers. Partial least squares regression (PLS) has been used for prediction of total VOCs using VOC analyser readings as training results. Each reading from the VOC analyser was assigned to its corresponding e-nose measurement, and the descriptor was recalculated from PLS regression. These statistical analyses were done by the e-nose built-in software (WinMuster, 2010).

4.3. RESULTS AND DISCUSSION

Selected physico-chemical characteristics of the biofilter media are shown in table 4.1. In general terms, the differences in compost properties were related to compost type (MSW or MSWP) showing both size grades of MSW composts higher pH, electrical conductivity, nitrogen content and bulk density than both grades of MSWP composts. All the composts kinds showed adequate pH for microorganism activity (pH 7 to 8) (Datta and Allen 2005), Higher bulk density of MSW composts could favour biofilter compaction.

Table 4.1.Characteristics of the compost-based biofilter filling media

Compost type		MSW2	MSW7	MSWP2	MSWP7
pH		7.63^{a}	7.50^{a}	7.23^{b}	7.20^{b}
E.C.[a] (1:5 extract)	$dS\ m^{-1}$	5.28^{a}	5.56^{a}	1.92^{b}	1.90^{b}
Organic Carbon	$g\ kg^{-1}$	123^{a}	180^{a}	383^{b}	484^{b}
Nitrogen	$g\ kg^{-1}$	15.3^{a}	13.1^{a}	11.9^{ab}	9.1^{b}
C/N		8.1	13.8	32.3	53.3
Bulk density	$kg\ m^{-3}$	485^{a}	354^{b}	269^{c}	233^{c}

[a] Electrical conductivity

Values in the same row followed by the same letter are not statistically different (Tuckey's HSD test, $p<0.05$)

The total-VOCs evolutions during one day period for the input and output air of biofilter MSWP2 are shown in fig. 4.2. Both sets of measurements were done on two consecutive days, starting after the wastes addition to the composter. These previous waste additions were 136 L day^{-1} (MSW + P) and 105 L day^{-1} in the case of input and output streams respectively. Average VOCs (24 h) concentrations for input and output air were 4,699 and 901 ppb_v respectively but several peaks and fluctuations were observed during the course of measurements due to composter turning and ventilation. Such fluctuations have also been observed during the compost transfer in the reactors (Ryu et al. 2011). The maximum VOC content for input air was 54,229 ppb_v and the maximum for output air was 17,372 ppb_v. These values were reached 12 h after waste additions, coinciding in time with a period of rotation of the composter and ventilation, which benefitted concentration of VOCs . Several authors detected maximum VOCs emissions during the first 48 h of composting and Pagans et al. (2006) indicating that such emissions were neither related to the biological activity nor the temperature. If both series of readings were compared, the (estimated) biofilter removal efficiency at the 12 h peak was lower than during the rest of the time. The decrease in removal efficiency under high VOCs loadings has been previously reported (Datta and Allen, 2005) and it could be due to a need of microorganism acclimatation (Kleinheinz et al., 1999). In these kind of systems subject to ample fluctuations, the monitoring of the concentration of VOCs by means of GC-MS systems could be difficult. To obtain reliable results, composite samples taken during a period of several hours or an elevated number of single time samples would be needed. In spite of its semi-quantitative character, the VOCs analyser could provide enough information on the overall biofiltration (or composting) process if extended sampling times is used.

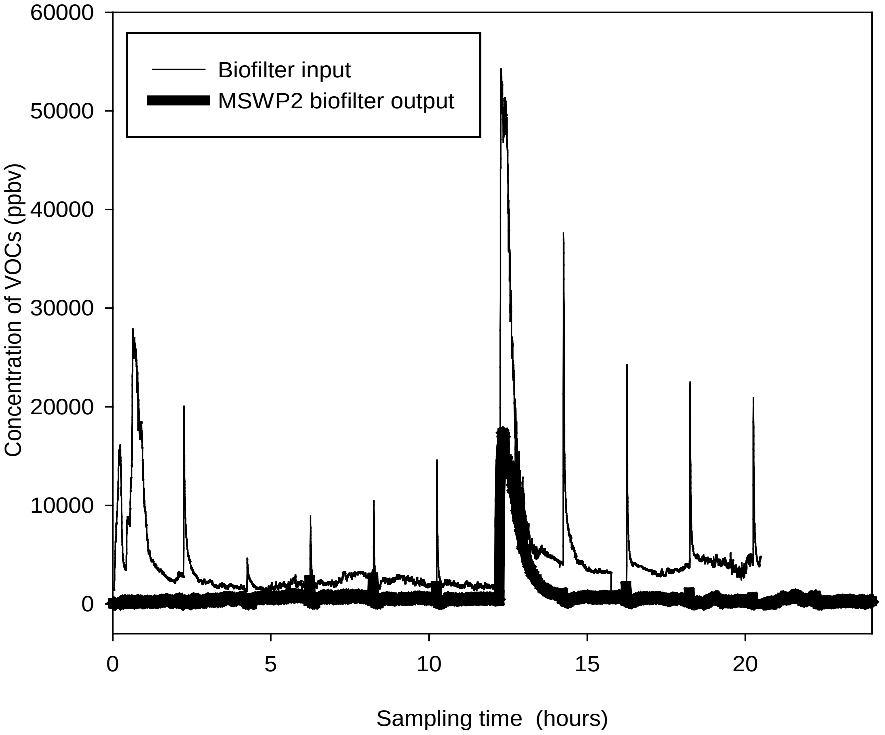

Fig.4.2. Daily evolution of concentration of total-VOCs in input and output air of MSW + pruning waste, particle size 2-7 mm (MSWP2) biofilter.

From total-VOCs readings, VOCs removal efficiencies for the 4 biofilter types were calculated (Table 4.2). These values should be taken with caution because the readings were obtained in a short sampling time. Regardless of compost type, the acclimatation period of the biofilters was about 5 days. Periods of acclimatation between 5 to 20 days are consistent with reported periods for compost biofilters (Hernández et al. 2010; Pandey et al. 2010; Raghuvanshi and Babu 2009). Efficiencies were greater than 90% on days 6 and 12 for which the concentrations of VOCs in input air were lower. Using biofilters with similar filling materials Pagans et al. (2006) found similar efficiencies (80-90%) treating gas from MSW composting. With respect to removal efficiency there is not clear differentiation that could be associated with biofilter nature or particle size.

Table 4.2.Concentration of VOCs in input air and VOC removal efficiency (%) for the different biofilter types.

Composting Day	1	5	6	12	20
Input air (ppb$_v$)	15595	4821	2725	3223	13650
MSW2	72.9 ^{a}	44.5 ^{a}	92.7 ^{a}	84.7 ^{a}	81.4 ^{a}
MSW7	67.3 ^{ab}	62.1 ^{b}	93.0 ^{a}	90.3 ^{ab}	82.0 ^{a}
MSWP2	51.7 ^{ab}	62.2 ^{b}	94.3 ^{a}	95.1 ^{b}	89.0 ^{a}
MSWP7	47.3 ^{b}	61.6 ^{b}	97.1 ^{a}	94.2 ^{b}	83.8 ^{a}

Values in the same column followed by the same letter are not statistically different (Tuckey's HSD test, $p<0.05$)

The biofilters performance over longer time periods could be altered by several factors such as clogging, changes in chemical properties (e.g. pH), poisoning due to chemical accumulation (e.g. NO_3^- or SO_4^{2-}) and this is not considered in this paper.

Considering separately e-nose data sets for each sampling day, Principal Component Analysis (PCA) revealed clear differences among biofilter input and output air (figure not shown). Fig. 4.3, shows the two principal components given by PCA applied to e-nose data corresponding to day 12 of composting, considering biofilter particle size (greater or lesser than 7 mm regardless of compost raw material, fig. 4.3A) or compost raw material (MSW or MSWP regardless of particle size, fig. 4.3B) as classes. Sample dilution factor was not included in the data set, taking into account that it was the same for the considered samples. On day 12 it was not possible to differentiate outlet air samples from the biofilters by compost size, but samples were separately grouped if compost raw material was the considered class factor. The MSW and MSWP groups were mainly separated along the y axis (function 2) which accounted for 17% of the variance. The loadings analysis of factors makes it possible to check the influence of each sensor on the distribution of data within the PCA-space. The loadings analysis showed that the sensor detecting methane-aliphatic compounds, the two sensors detecting sulphur organic compounds and the broad range sensor accounted for the grouping difference along the y axis. At least at this stage of the composting process, the origin of the biofilter materials seemed to have a moderate influence over the composition of VOCs in the output air.

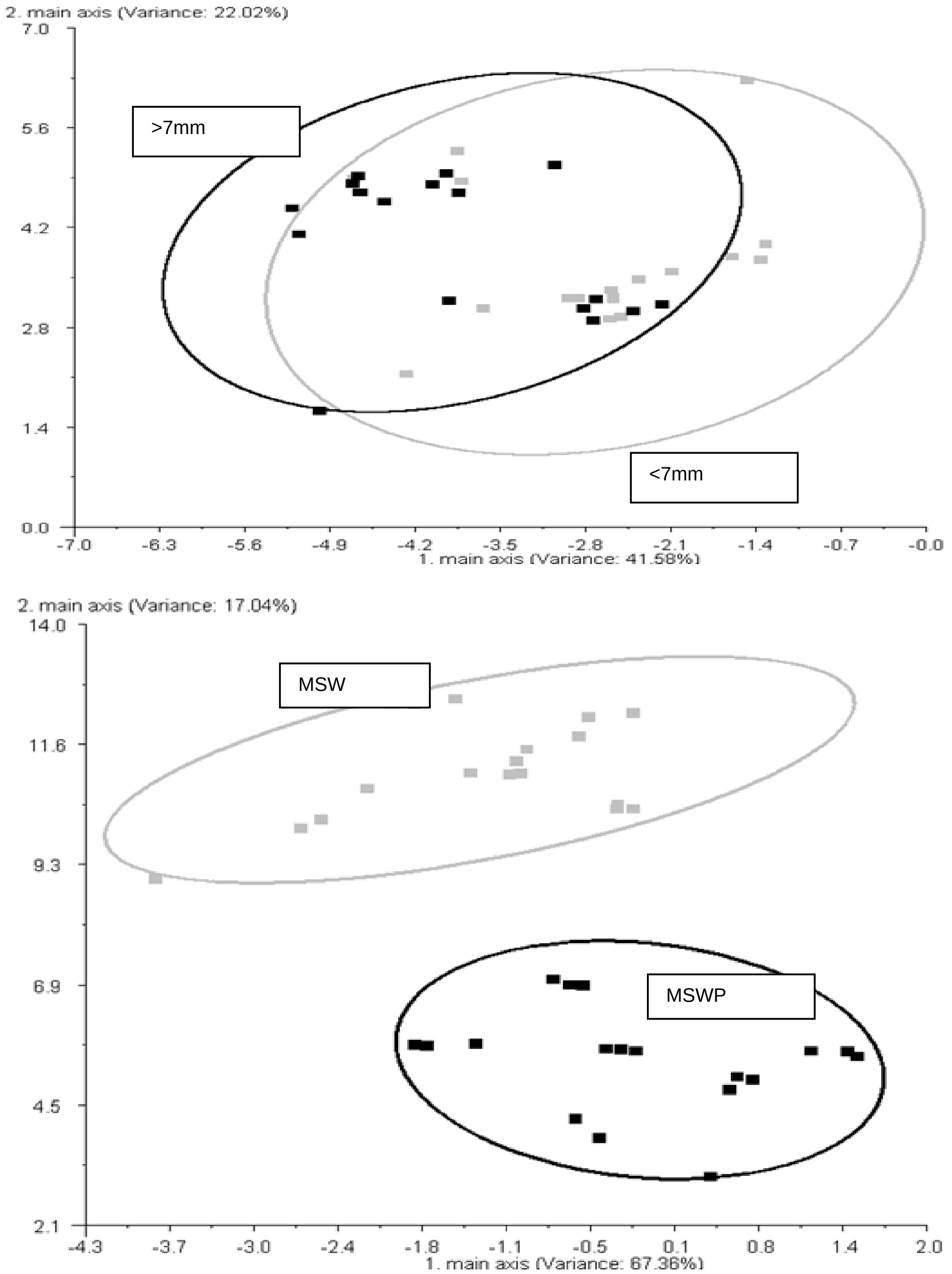

Fig. 4.3. Principal Component Analysis plots considering particle size (A) or compost type (B) as classification factor in samples corresponding to day 12 of composting. Wrapping lines correspond to Hem classes.

PCA analysis of samples on day 12 of composting, considering for classification the four composts used, is shown in fig. 4.4. Based on the pattern including the data of the 10 e-nose sensors (fig. 4.4 A), the loading analysis showed that sensors that mainly detected sulphur-organic, sulphur-chloride and methane-aliphatic compounds respectively were the more discriminating ones. These results agreed with the content of the sulphur-compounds (sum of dimethylsulphide and dimethyldisulphide) determined by GC-MS on day 20 which were 2.3 times higher in MSW biofilters than in MSWP biofilters (López et al., 2010). Both sulphur compounds, dimethylsulphide and dimethyldisulphide, were frequently found in the air emissions of composting facilities (Müller et al., 2004; Smet et al., 1999; Tsai et al., 2008). If only the responses corresponding to these 3 sensors are selected for the PCA, a better resolution among classes was observed (fig. 4.4B). The associated variance to the two principal components in PCA was also improved (84.4 % with 10 sensors, 99.9 % with 3 sensors). From the fig. 4.4B, it can be concluded that the air from small-grained biofilters, MSW2 and MSWP2, appeared quite different between them and in the same way, the air from the coarse-grained biofilters (MSW7 and MSWP7), was more similar among them. Both factors, compost origin and particle size seem to have affected the composition of VOCs of the output air. The readings of total-VOCs corresponding to these samples were in the order of one to seven hundred ppb$_v$ and therefore, the electronic nose was able to detect very small differences in air composition.

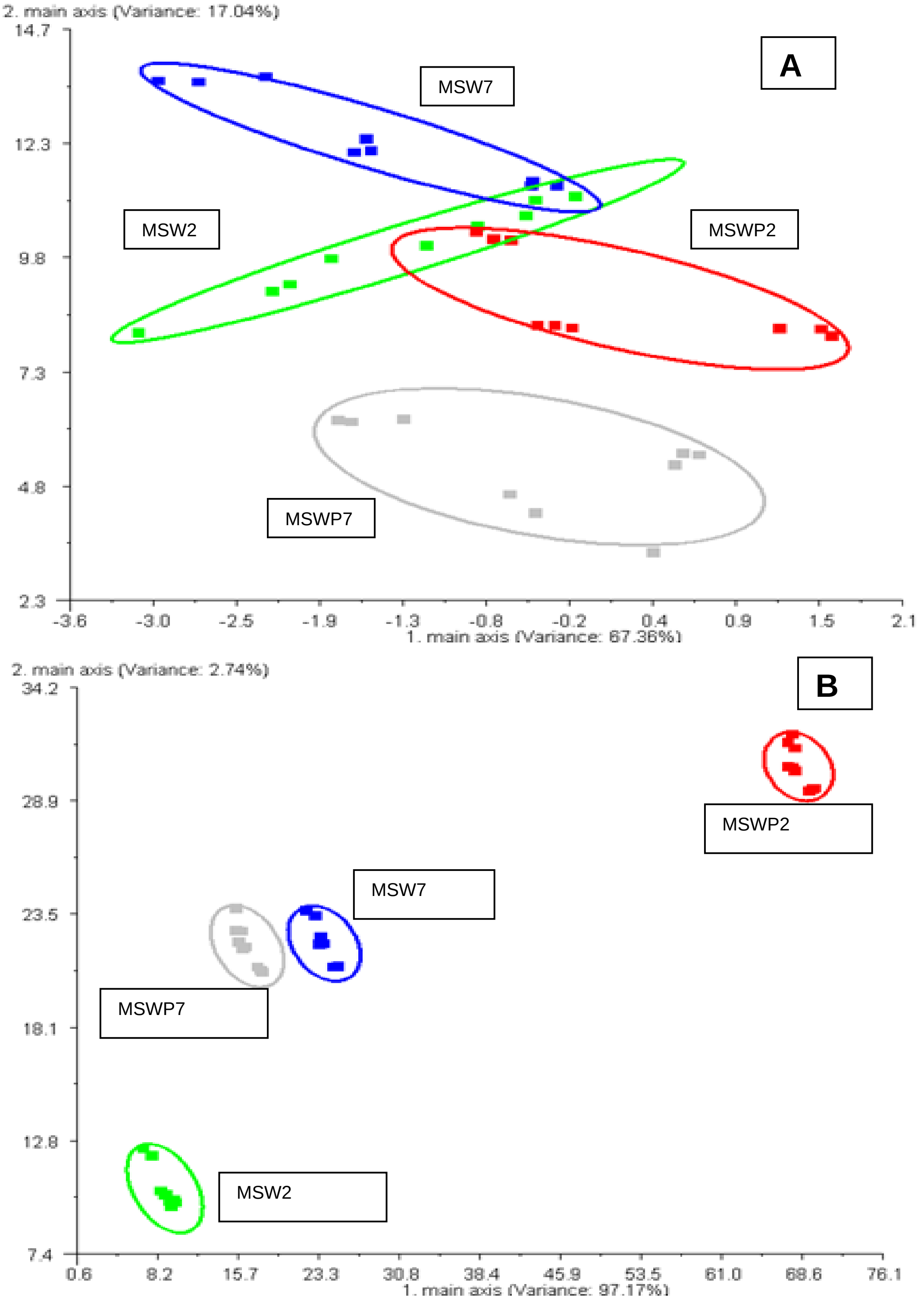

Fig. 4.4. Principal Component Analysis plots considering the four compost types as classification factor. Analysis considering 10 sensor data (A) and 3 selected sensor data (B) on day 12. Wrapping lines correspond to Hem classes.

It was not surprising that the e-nose detected such differences (input air-output air, biofilter type), since if you consider the data collected in only one day, the situation can be described as relatively static. Ljungberg Willing et al. (1998), compared human and electronic responses to paperboard odour and they found that some e-nose sensors can be correlated with a selected group of odour descriptors determined by a panel. Sironi et al. (2007) found coherency between the odour detections with an e-nose and the material turning or moving operations inside a composting plant, at least during a short period of 5 days. Using a similar e-nose Littarru (2007) detected qualitative differences between biofilter emissions related to the age of the composting waste. Besides , there are no previous papers which reported, using an e-nose, such differences comparing similar biofilter materials at these low concentrations of total-VOCs .

The complete data set including the samplings corresponding to 1, 5, 6, 12 and 20 days of composting was also studied. In spite of the evolution of composting, which originates differences in the composition of exhaust gases, several patterns could be successfully applied. PCA on fig. 4.5A showed good separation if biofilter input (32 samples) and output air (135 samples) are the considered classes. Only 6 sensor signals and the dilution factor were used in this statistical analysis. The less loading sensors in the distribution were those more nonspecific, detecting a broad range of compounds.

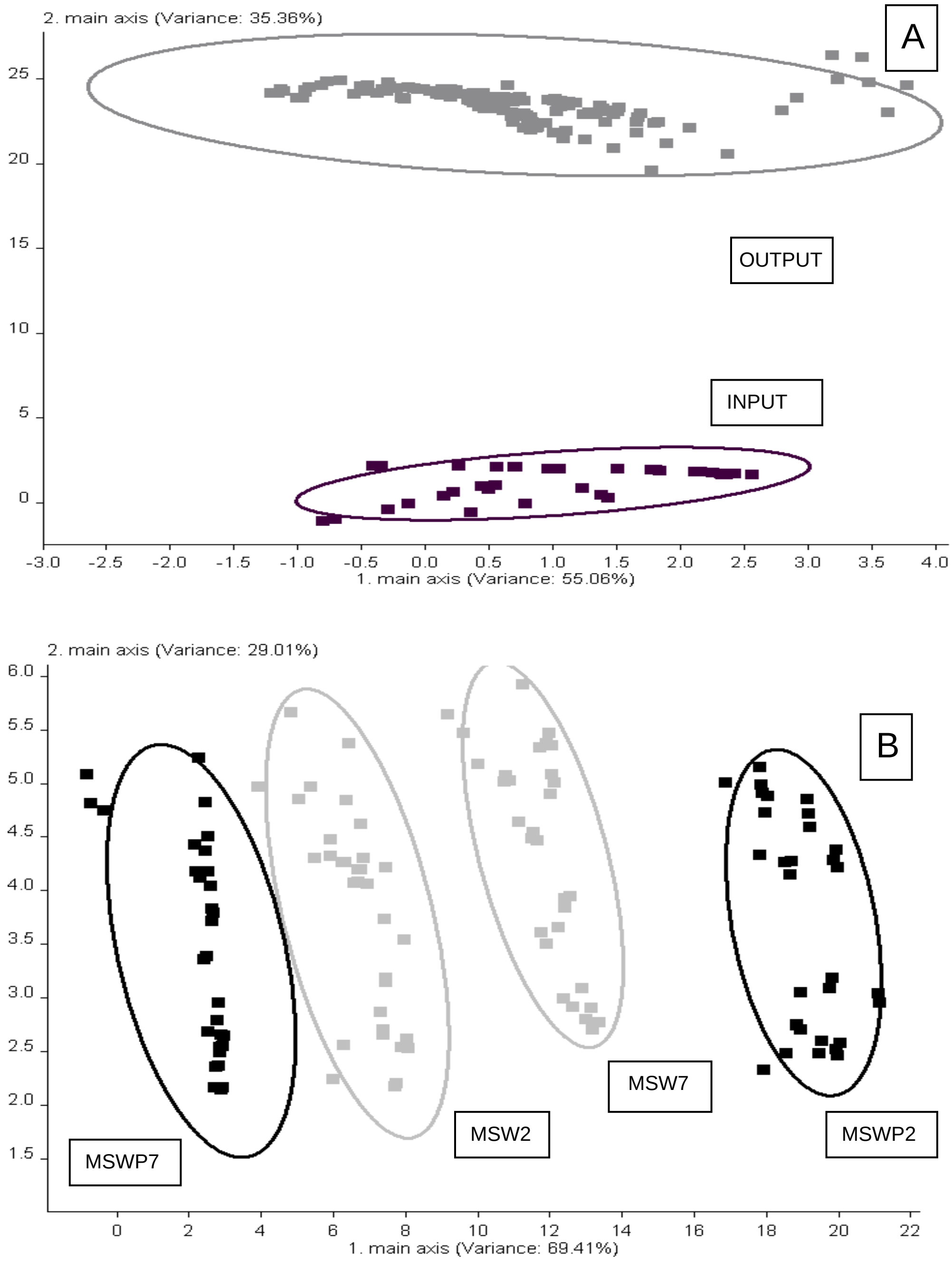

Fig. 4.5. Principal Component Analysis plots for the whole composting process. A: Classes are biofilter input and output air; data set: 6 sensors and dilution factor. B: Classes are the 4 types of compost in biofilter; data set: 3 sensor data and dilution factor. Wrapping lines correspond to Hem classes.

The 6 sensors selected corresponded to those more specific to aromatic compounds (2 sensors), aromatic-aliphatic compounds (1), sulphur-organic (1) sulphur-chloride compounds (1) and to hydrogen (1). These families of organic compounds have been usually detected in composting gases. Müller et al. (2004) in the air near municipal biowaste and plant refuse composting facilities detected some terpenoids (limonene, α-pinene, camphene, camphor and carene), aliphatic alcohols (3-methyl-1-butanol and 2-methyl-1-butanol), ketones (3-octanone and 2-heptanona) and dimethyldisulphide between the most abundant compounds. Mao et al. (2006) in the ambient air of a food waste composting plant found amines, dimethylsulphide, acetic acid, aliphatic and aromatic hydrocarbons (styrene, toluene), ketones, esters and the terpenes. GC-MS determinations carried out on day 20 of composting detected that the terpenes α-pinene, β-pinene and limonene dropped significantly from input to output air, being 95.8 % the average removal efficiency in the biofilters (López et al., 2010). From the previous input-output pattern and using euclidean distance and correlation classifiers only 8 from the 167 samples were incorrectly assorted. This pattern even classified correctly 34 of 36 biofilter output samples and 3 of 3 input samples corresponding to a next composting trial, performed one year after.

If the biofilter particle size (greater or lesser than 7 mm) or compost raw material (MSW or MSWP) were chosen for the classification, the distinction between classes was not evident (figure not shown), but PCA could separate the 4 biofilter types (128 samples included, 7 outlier samples corresponding to day 20 excluded) from the analysis. The reason why the samples on day 20 were outliers is probably related to the intense and perceptible ammonium smell, coming from fish residues incorporated to the composter the previous days. The discrimination among compost types improved only if more loading sensors were selected: hydrogen, sulphur-organic, sulphur-chloride and also the dilution factor (fig. 4.5B). The total variance associated to the main two vectors also improved to 98.4 %, with 69.4% of variance corresponding to the function 1 (horizontal axis) in which classes differentiation was more evident. The compost beds including pruning waste showed substantial differences, and in the opposite case, both particle sizes of MSW composts were less dissimilar between them according to the PCA analysis indicated above. Using the euclidean distance as classifier, all 128 samples were correctly assigned to the biofilter type. The correlation classifier permitted the correct classification of 126 samples.

In general terms, during a lasting composting period, the air composition could be time-dependent and the observation of classes differences from the PCA could become difficult. Rajamäki et al. (2005) observed that only after 13 days of composting air samples from aerobic and anaerobic composters started to separate and they concluded that it was possible to distinguish aerobic and anaerobic conditions using the e-nose after 27 days of composting. In the current experiment differences in air composition were related to the composting time but also, and probably in a greater extension, to the biofilter type and activity, which permitted the separation of the four groups of biofilters when using the complete period of observations.

The correlation between predicted and determined concentrations of VOCs was done by PLS using the data sets separately corresponding to days 1 and 12 of the composting process. In the case of day 1, both input and output biofilter air samples were included in the regression. In the case of day 12, only four types of output air samples (type of compost bed) were used in the PLS procedure. On both days (data not shown) the regression slope was very close to 1, and the regression was significant, but on day 1 the deviation between some predicted and determined values could reach ±30%. On day 12 the coefficient of determination (r^2=0.957) was greater than the corresponding to day 1 (r^2=0.733). The concentrations of VOCs on day 12 were below 1 ppm_v indicating the high sensitivity of e-nose sensors to detect small changes in gas concentration. The better fitting of the regression on day 12 than on day 1 was relatively surprising taking into account that VOCs readings on day 1 (in the range of a few ppm_v) were about 10 times the readings on day 12 (a few hundreds ppb_v). Littaru (2007) and Sironi et al. (2007) also found a good relationship between sensor signal and odour concentration if diluted samples (in the range 30-100 ou_E m^{-3}) were used as a training data set. Sironi et al. (2007) justified the choice of a narrow concentration range by the fact that the relationship sensor signal-concentration is not linear. In the present case, there is not evidence that the regression corresponding to day 1 (not shown) follows a different pattern (i.e. a logarithmic relationship). Humidity or temperature variations can also produce some bias both in PID-VOCs readings or e-nose measurements. The biofilter input and output samples on day 1 varied in temperature, humidity and qualitative composition, but if the readings corresponding to input samples are excluded from the regression it does not improve. At least to some degree, the point scattering on day 1 (indicated by the r^2=0.733) could be related to a quick change in air composition or biofilter activity due to the incipient biofiltering process.

The PLS analysis has been also applied to the combined data sets of days 1, 12 and 20, considering the output biofilter samples distributed in the 4 types of composts beds (80 samples). Complete data set from each e-nose measurement (10 absolute sensor signals and dilution factor) was used for PLS regression. The optimal number of latent variables in this model was 9, 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. measured VOC concentrations are shown in the fig. 4.6. The linear relationship previously obtained for single day data sets was also displayed for the combined data sets, although for the lower concentrations of VOCs (ca. <1000 ppb_v) the predicted values could be inaccurate, and even negative values could be obtained (detail drawing in fig. 4.6). For such a situation a PLS analysis limited to a reduced VOCs range could offer a better prediction. Studying anaerobic digestion Orzi et al. (2010) found significant correlation between electronic nose measurements and odour in samples with a similar c concentration of VOCs(1000-6000 ppb_v) to those found in the present study. The work by Orzi et al. (2010) is one of the few cases in which such correlations have been reported for a relatively dilated sampling period (57 days). The range of extension of the lineal relationship (12,000 ppb_v) in the present study indicates that e-nose sensor response did not suffer saturation effects at least in the considered amplitude.

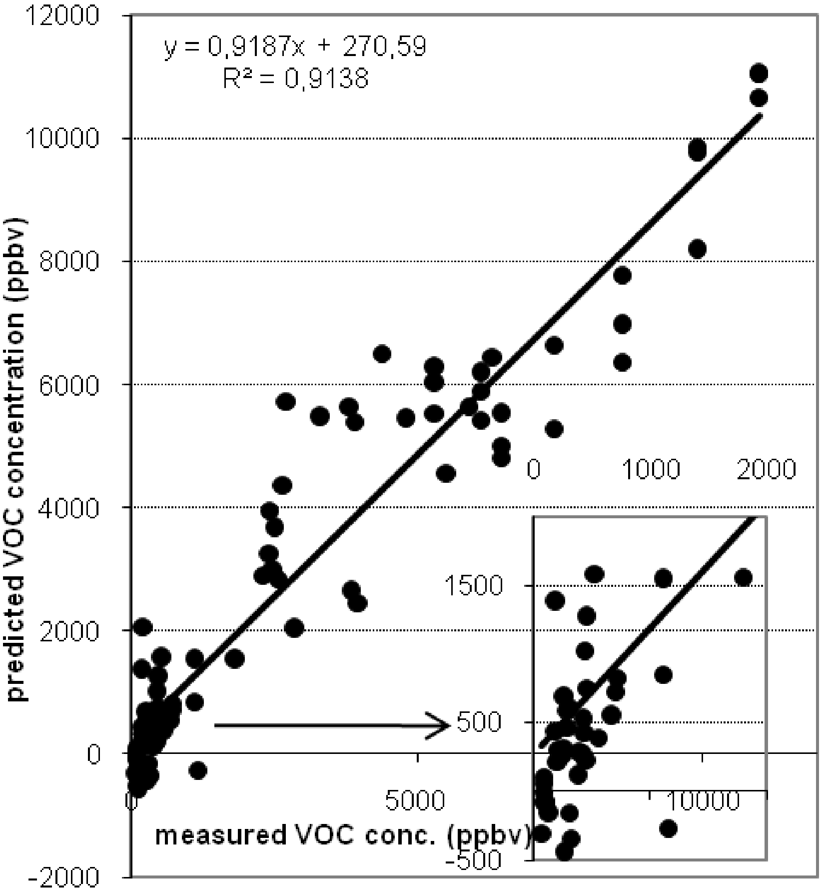

Fig. 4.6. Measured concentration of VOCs vs. PLS predicted from e-nose values for combined data sets of composting days 1, 12 and 20.

4.4. CONCLUSIONS

VOC removal efficiencies of the biofilter media were affected by the input fluctuations due to the rotation and aeration of the drum composter. The biofiltering process of the emitted gases by different MSW or MSW-pruning waste compost reached VOC removal efficiencies greater than 90%.

The e-nose could identify qualitative differences among the biofilter output gases at very low concentration of VOCs related to compost nature and, compost particle size. Sensors detecting sulphur containing-compounds were especially discriminating. The e-nose could also be used to quantify total-VOCs content in air samples during a 20 day composting and biofiltering trial.

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5. BIOFILTRATION OF α-PINENE VAPOURS USING MUNICIPAL SOLID WASTE (MSW) – PRUNING RESIDUES (P) COMPOSTS AS PACKING MATERIALS

5.1. 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, stock piling, etc. 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 (Pagans et al., 2005; Tsai et al., 2008). The most important group of chemicals responsible for this odour are VOCs and some inorganic gases (ammonia, hydrogen sulfide, etc) produced during the biodegradation of organic residues (Beck-Friis et al., 2001; Delgado-Rodríguez et al., 2010; Müller et al., 2004; Stoffella & Kahn, 2005). The family of terpenes is one of the most representative classes of VOCs emitted during the degradation process of vegetal materials (chips, grass clippings, pruning residues, etc). Amongst them, α-pinene is frequently the predominant compound, representing between 10.2 and 72.7 % of the total emissions (Büyüksönmez & Evans, 2007). Furthermore, α-pinene is also emitted by wood processing industries, in particular, saw mills, composite board mills, and paper industries (Mohseni & Allen, 2000; Van Groenestijn & Liu, 2002). Although, the optimization of the operational parameters of composting processes is an important objective for the scientific community in order to reduce the VOC´s emissions (Delgado-Rodríguez et al., 2010; Delgado-

Rodríguez et al., 2011); 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. (Namkoong et al., 2003; Revah & Morgan-Sagastume, 2005; Schlegelmilch et al., 2005).

Biofiltration is considered to be an advantageous system for deodorisation due to low operating costs and their abilty to treat large volumes of waste gas streams containing low concentrations of odorous compounds (Dorado et al., 2010; Mudliar et al., 2010). 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 (Datta & Grant-Allen, 2005). 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 (Miller & Allen, 2005), the solubility of the compound in water is a limiting factor in the process. For this reason, the study and optimization of hydrophobic compounds treatment, using biofiltration technology is a challenge for the scientific community (Mohseni & Allen, 2000; Paca et al., 2010; Vergara-Fernández et al., 2012).

α-pinene, one of the major hydrophobic compounds, was selected as the marker VOC in this study. Considering the low solubility of α-pinene in the water phase (2.5 mgl^{-1} at 23ºC) (Bagherpour et al., 2005; Dhamwichukorn et al., 2001), it was interesting to evaluate the treatment of this contaminant through biofiltration technology. Biofilter monitoring is usually carried out using GC/MS and olfactometric techniques when an evaluation of the odours is required (Chen et al., 2008; Delgado-Rodríguez et al., 2011; Dever et al., 2007; Romain et al., 2009).

The use and advantages of e-noses have already been widely reported in order to evaluate the presence of VOCs and odours (Delgado-Rodríguez et al., 2012; Littarru, 2007; López et al., 2011; Rajamäki et al., 2005; Stuetz & Nicolas, 2001). 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 (Hobbs et al., 1995; Karlik et al., 2002; Muñoz et al., 2010; Smith et al., 2007). 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) (López et al., 2011).

This study focused on the evaluation of the VOCs removal efficiency for biofilters that used compost either MSW and MSW-Pruning residues as the packing material. The biofilters treated an artificial stream of gases containing a hydrophobic VOC (α-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.

5.2. MATERIALS AND METHODS

5.2.1. BIOFILTRATION UNIT

The biofiltration system consisted of two laboratory scale biofilters (Fig 5.1.), 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 5.1., additional details can be found in Delgado-Rodriguez et al. (Delgado-Rodríguez et al., 2010).

Table 5.1. Relevant physic-chemical properties of the packing materials used in the biofiltration system proposed (over dry basis) (average ± standard deviation [a]).

		MSW[b]	*MSW-P*[b]
pH (1:5 extract)		6.55 ± 0.2	5.60 ± 0.1
EC (1:5 extract)	mS m-1	12,45 ± 0.1	11,57 ± 0.1
Organic Matter	g kg-1	301 ± 82	842 ± 93
Kjeldahl-N2	g kg-1	14.1 ± 1.4	11 ± 0.4
C/N		12.55	45.03
Bulk density	g L-1	705 ± 50	374 ± 54

[a] Average ± standard deviation, over four samples, (d.w.)
[b] MSW: Municipal solid waste composts; MSW-P: Municipal solid waste – Pruning residues composts

The granulometry of both packing materials was from 7 to 20 mm, in order to improve removal efficiency and avoid operational problems (clogging, control of air flux, etc). The packing materials had previously been used to treat a gas stream composed of a VOC mixture from the active composting of MSW for up to two months (López et al., 2011). 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 ºC. 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.w) to be able to compare each medium.

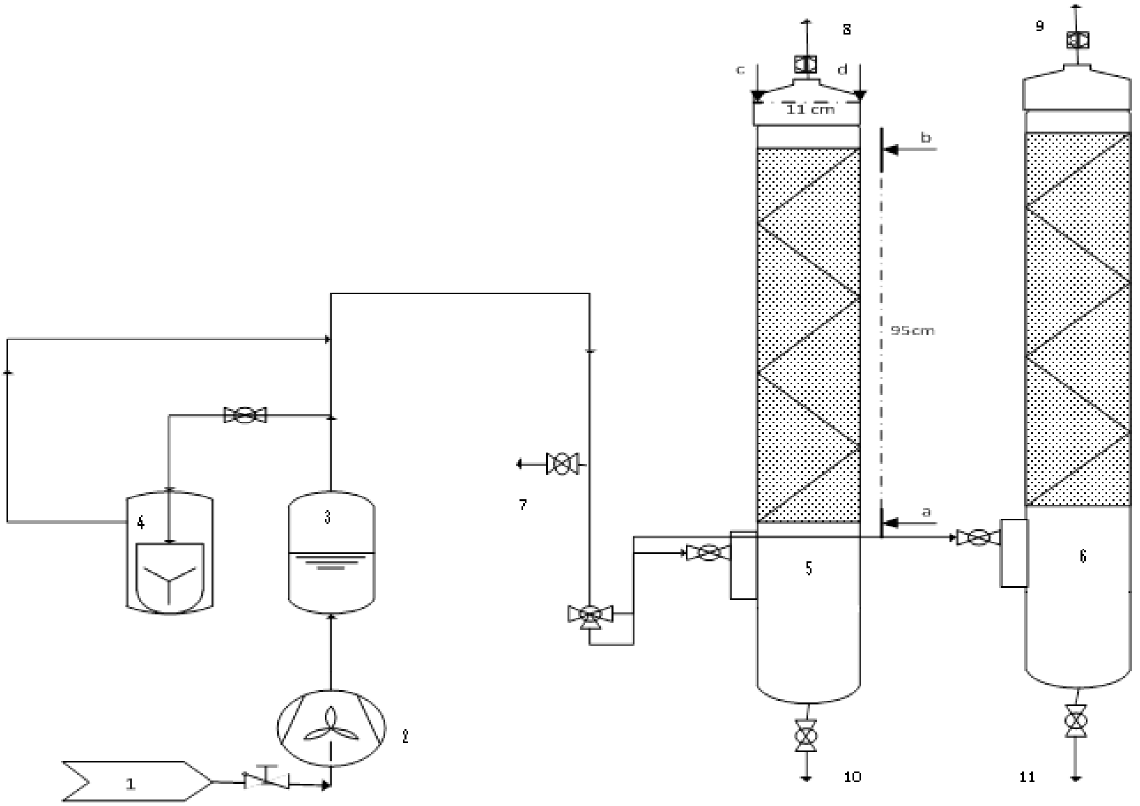

Figure 5.1. Schematic diagram of the biofiltration system. (1) Pressurized air; (2) Compressor; (3) Humidifier; (4) α-pinene sparger; (5) Biofilter compost MSW; (6) Biofilter compost MSW-P; (7) input sampling port; (8,9) outlet biofilter gas/output sampling port; (10,11) Water drainage

The inlet gas stream was supplied from the bottom of the column (ascending flow). Pressurized ambience air was obtained using a compressor of oil-free products; the air was taken from the surroundings with the purpose to operate continuously and to facilitate the following humidification process of the air. Depending on the stage of the experiment, the inlet gas was humidified to 90-100% relative humidity, by sparging the gas stream through a reservoir filled with water. In order to generate the contaminated airflow, a small fraction of humidified air was fed to a sparger, which contained liquid α-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 α-pinene; guaranteeing the concentration of the contaminant fixed during 6 to 8 hours. The average α-pinene concentration during all the stages of the experiment was 11.6 ppm_v . 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 (Box & Behnken, 1960; Dorado et al., 2008; López et al., 2011; Omri et al., 2011; Ramírez et al., 2011).

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

5.2.2. *VOCS ANALYSER MEASUREMENTS*

Rapid *in situ* measurements of the α-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 (Fig.5.1.). The instrument sensitivity was 0.1 ppm_v in a concentration range from 0 ppm_v to 200 ppm_v. The suitability of this instrument for semi-quantitative measurements of VOCs has been reported in a number of studies (Delgado-Rodríguez et al., 2010; Karlik et al., 2002; Ojala et al., 2006). As α-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 α-pinene concentrations using a correction factor of 0.31 (RAE_Systems, 2002).

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 $Lmin^{-1}$. 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 (Ojala et al., 2006). For this reason, a teflon filter (0.2 µm pore size) was used as a water and particulate material trap. The removal efficiency was determined as present in the following equation (Eq.1):

$$RE = \frac{(C_{in} - C_{out})*100}{C_{in}} \quad \text{(Eq. 5.1)}$$

Where, RE: removal efficiency (%); C_{in} : Inlet α-pinene concentration (ppm); C_{out}: Outlet α-pinene concentration (ppm).

5.2.3. *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 was 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 α-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-nose´s built-in software (WinMuster_1.6.2.14, 2010).

5.2.4. *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 (Bio1) and MSW-P biofilter (Bio2), using tedlar bags with a capacity of 3 L. Samples were stored at room temperature in darkness for 24 hours 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 prior to its analysis using the solid phase microextraction method. A SPME fibre coated with 75 µm carboxenpolydimethylsiloxane (Supelco, Bellefonte, PA, USA) was used to capture VOCs in the tedlar 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 ºC 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 ºC 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 5.2.

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

Type	Shimadzu GCMS-QP2010SE		
Injecting port	Split less		
Injector temperature	250 ºC		
Detector temperature	230 ºC		
Capillary column	HP-5MS (Agilent) 30m x 0.25 mm i.d. x 0.25µm		
Column linear velocity	36 cm/sec. (1 mL/min)		
Oven Program			
Initial temperature	35 ºC		
Initial time	5 min		
	Rate (ºC/min)	Final temp (ºC)	Final time (min)
	5	270	20
Mass Spectrometer			
EI voltage	70 eV		
Mass range, scan mode	m/z 30-550 amu		
Solvent delay	0 min		

5.3. *RESULTS AND DISCUSSION*

The α-pinene concentration in the inlet gas stream was maintained during a period of 5 to 10 hours each day, depending on the stage of the experiment. Fig. 5.2. shows the tendency of the VOCs detector signal observed during the complete experiment. The highest concentration reached was 3 ppm_v, which corresponds to the acclimatization phase of the biofiltration system. All measurements were performed when the signal of the VOC´s detector was constant, as shown in Fig. 5.2., so that results could be compared.

Fig. 5.3. represents the α-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 % (dw) and 100%-89% (dw) for biofilter 1 (Bio1) and biofilter 2 (Bio2), respectively. During this period, the acclimatization of the system occurred; Bio1 needed approximately 10 days to reach α-pinene removal efficiency greater than 90 % whereas Bio2 removal efficiency reached 80 % after 25 days. These acclimatization periods were longer than those reported in previous studies (Bagherpour et al., 2005; Mohseni & Allen, 2000; Pandey et al., 2010). Bagherpour et al. (Bagherpour et al., 2005) attributed the short acclimation time to the fact that the compost and wood chips used (as packing materials) had been aged for six months, allowing the production of terpenes and the appearance of microorganisms adapted to this carbon source. In this case, the packing materials had also been used before to treat exhaust gases coming from kitchen waste and pruning residues composting (López et al., 2011), which suggests that the microbial community present in the packing material had adapted to the α-pinene. The longer acclimation period found in our study is

possibly due to the inactivation of the microbial community as a consequence of the moisture reduction, which occurred in the packing materials between the experiments. On the other hand, Jin et al. (Jin et al., 2007) reported acclimation periods of 28 days before complete removal of α-pinene took place whereas Van Groenestijn and Liu (2002) found acclimation periods from 4 to 8 weeks, indicating that start-up periods between 10 and 25 days must be considered as normal in biofiltration systems using natural packing materials.

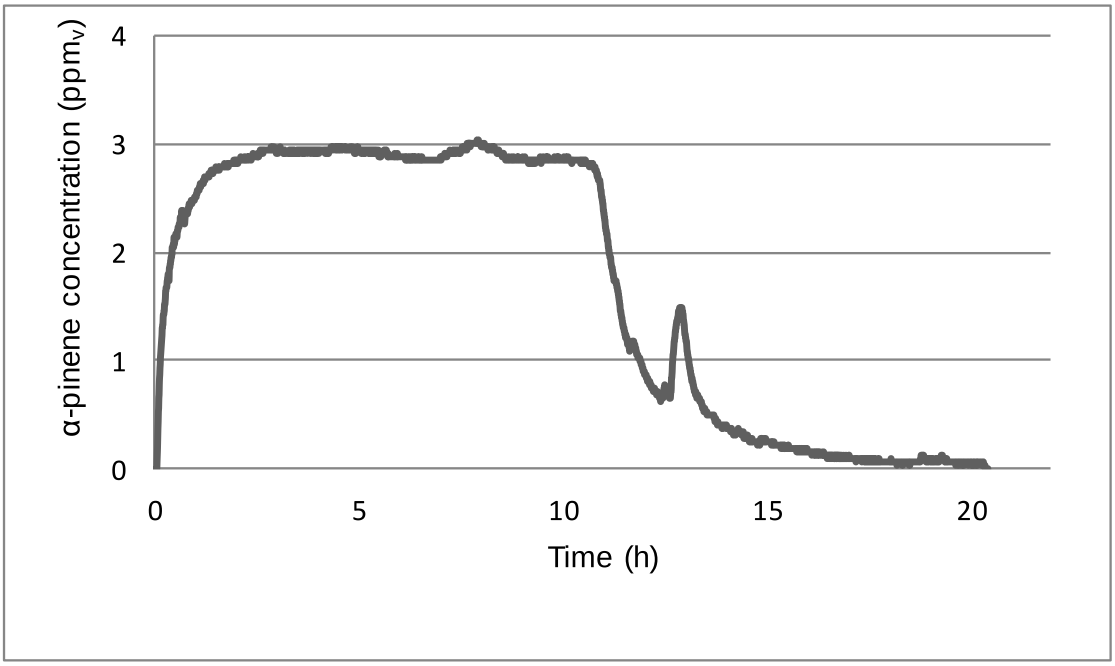

Figure 5.2. Evolution of the α-pinene concentration in the inlet stream during the acclimation phase of the biofiltration system

In the 2nd experimental stage (days 80-144), the α-pinene concentration in the inlet gas stream was progressively increased to a maximum of1800 ppm$_V$. The removal efficiency of the biofilters decreased to below 90 % as α-pinene concentrations was increased over 30 ppm$_V$. Fig. 5.3. shows a significant decrease in the removal efficiency as soon as the α-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 (Kleinheinz et al., 1999).

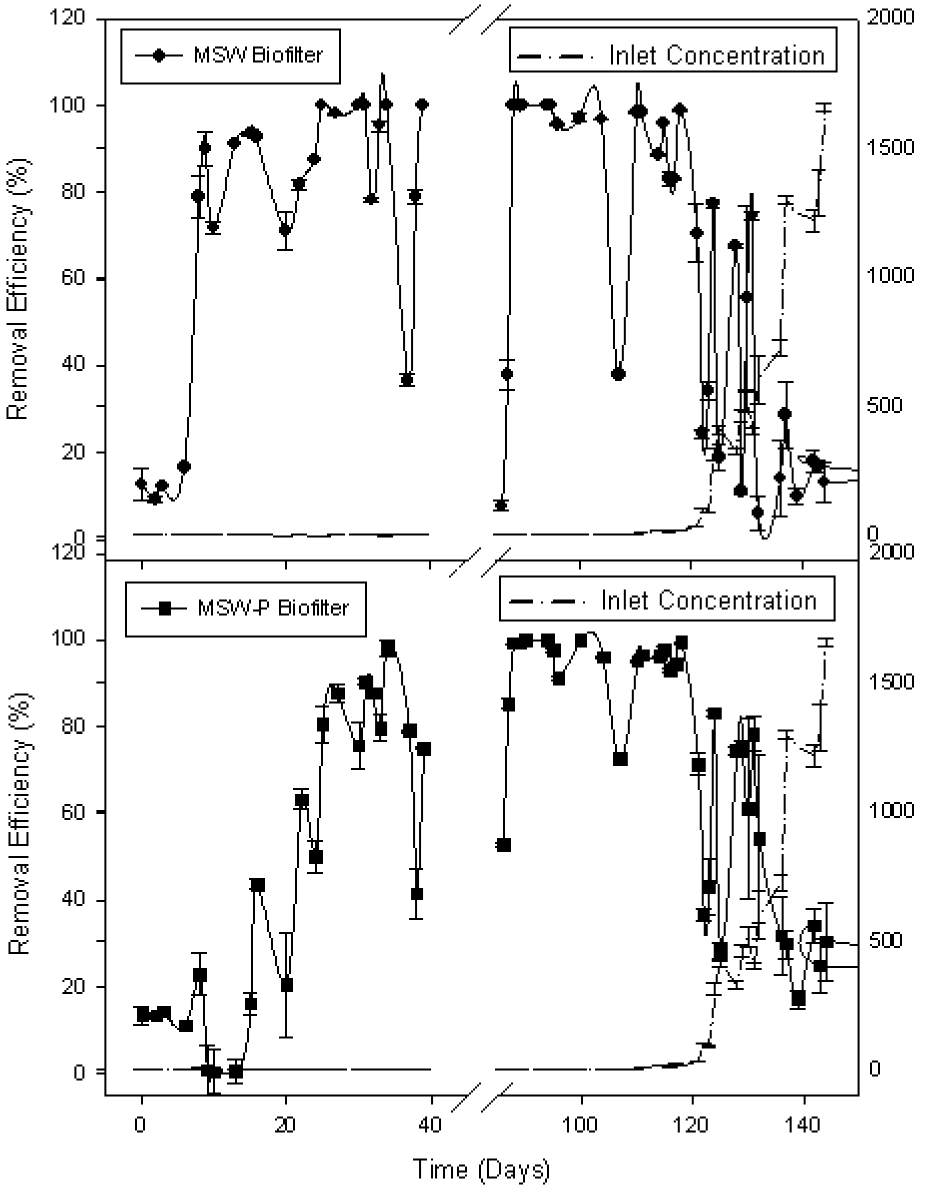

Figure 5.3. Removal efficiency (%) and inlet concentration (ppmv) of α-pinene in the biofiltration system proposed during the first 140 days of the experiment

After a sharp decline of the efficiency in the system occurred on day 121 (Fig. 5.3.), which corresponded to the higher inlet concentrations, improved performance was observed for the treatment of α-pinene by Bio2. Specifically, when the concentration of the compound in the inlet gas stream was 672 ppm_v, the average efficiency was 33.8 % and 48.4 % in Bio1 and Bio2, respectively. These figures corresponded to an elimination capacity of α-pinene by the system of 79 $g.m^{-3}$ bed $media.h^{-1}$ (Bio1) and 113 $g.m^{-3}$ bed $media.h^{-1}$ (Bio2). Mohseni and Allen (2000) and Mohseni et al. (Mohseni et al., 1998) reported lower elimination capacities (40-45 and 30-35 $g.m^{-3}$ bed $media.h^{-1}$) for α-pinene using similar packing materials, with EBRTs of 20 and 45 s, and inlet concentrations of 109 ppm_v and 40 ppm_v, respectively. Similarly, Bagherpour et al. (Bagherpour et al., 2005) reached values for this efficiency parameter of 210 $g.m^{-3}$ bed $media.h^{-1}$ with an inlet α-pinene concentration of 114 ppm_v. However, no previous studies have reported inlet α-pinene concentration that are greater than or equal to the maximum used in this study, suggesting that the proposed biofiltration system would enlarge the range of working concentrations.

In the third phase of the experiment, from day 154 to day 184 (Fig. 5.4.), the moisture content of the packing materials was reduced progressively by eliminating the humidification unit. The inlet α-pinene concentration was also set at 17 $ppm_{v,}$ 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 acclimatization. After this period, when the moisture content was 77% (d.w) and 91 % (d.w) for the Bio1 and Bio2 respectively, the removal efficiency for both biofilters was 100

% (Fig. 5.4.). The biofilter performance however was adversely affected when the moisture content of the packing materials was set below 66 % for Bio1 and 51 % for Bio2 with removal efficiencies observed to be lower than 90 %.

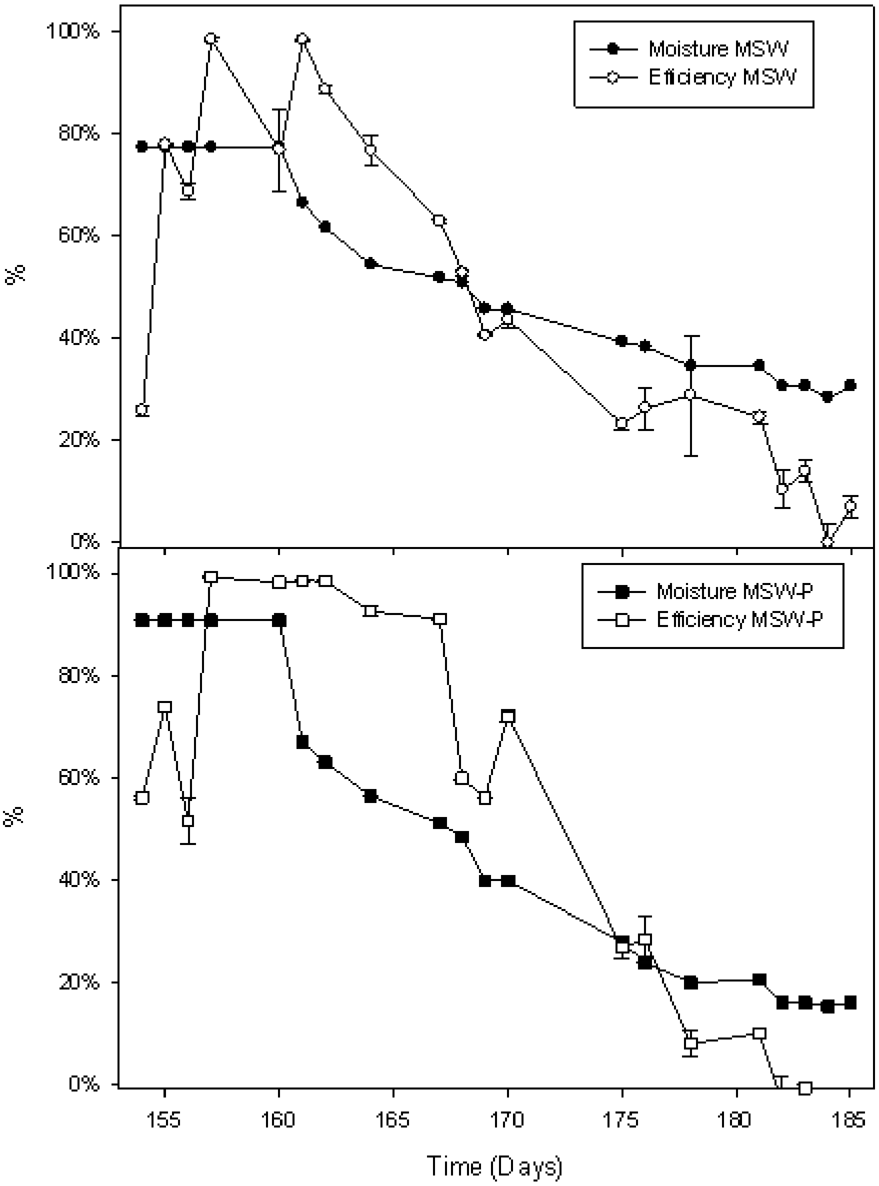

Figure 5.4. Biofiltration system performance during the decrease of the moisture content of the packing materials

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.w) in the case of the Bio1 and between 51 and 100 % (d.w) for Bio2, respectively. These results are consistent with those found in previous studies (Morales et al., 2003), where the minimum moisture content suggested for the packing material was reported as 66 % (d.w).

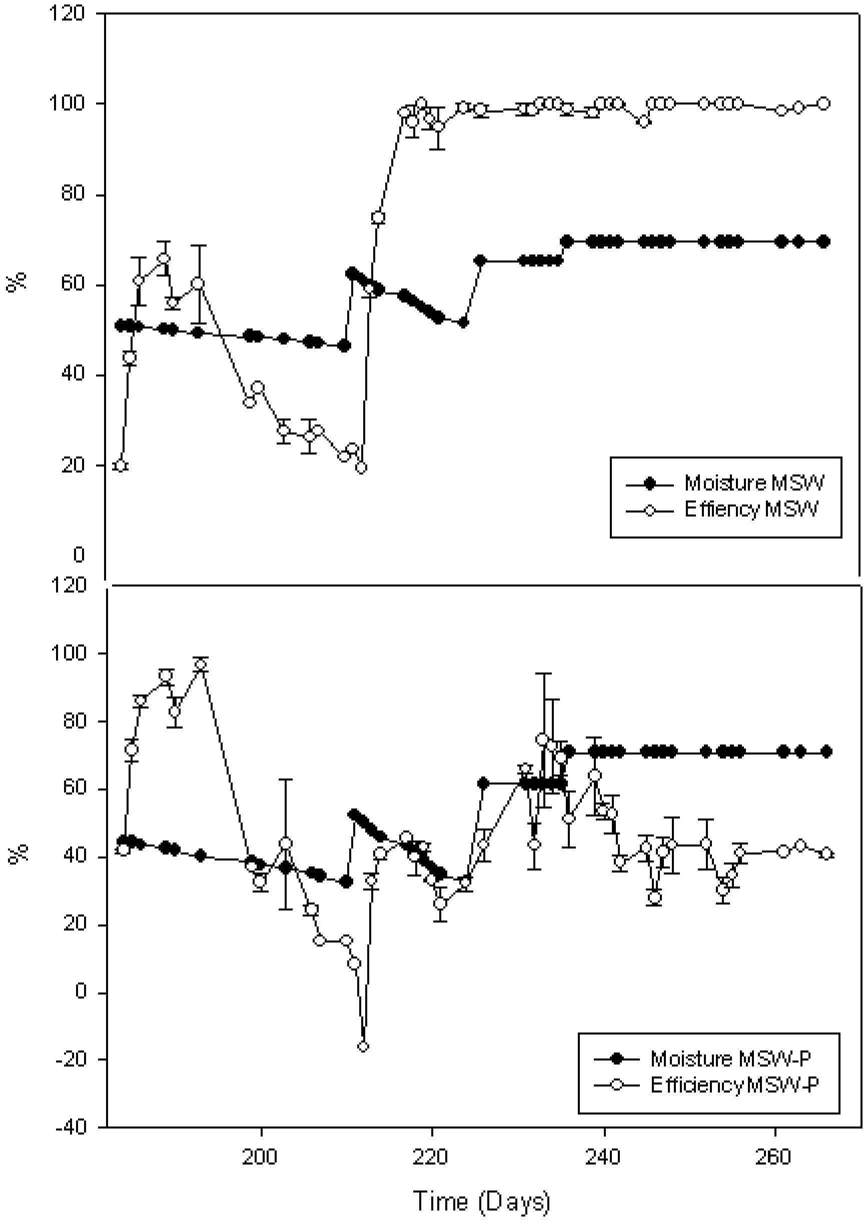

Figure 5.5. Assessment of the biofilters adaptation capacity during the replacement stage of the beds moisture content

The four study stage was carried out between day 185 and day 266 (Fig. 5.5.). 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 α-pinene during this stage was 11.6 ppm_v. Although the moisture content of both packing materials was adjusted progressively to the optimum range found in the previous stage; only Bio1 was able to reach a removal efficiency of 100 %, whereas Bio2 removal efficiency stagnated at a value around 40 %. It is noticeable that the 100 % of removal efficiency in Bio1 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. 5.6. 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 (López et al., 2011). Although almost all VOCs found in this sampling were previously reported as common emissions in composting processes (Delgado-Rodríguez et al., 2011), 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 came 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 fibers.

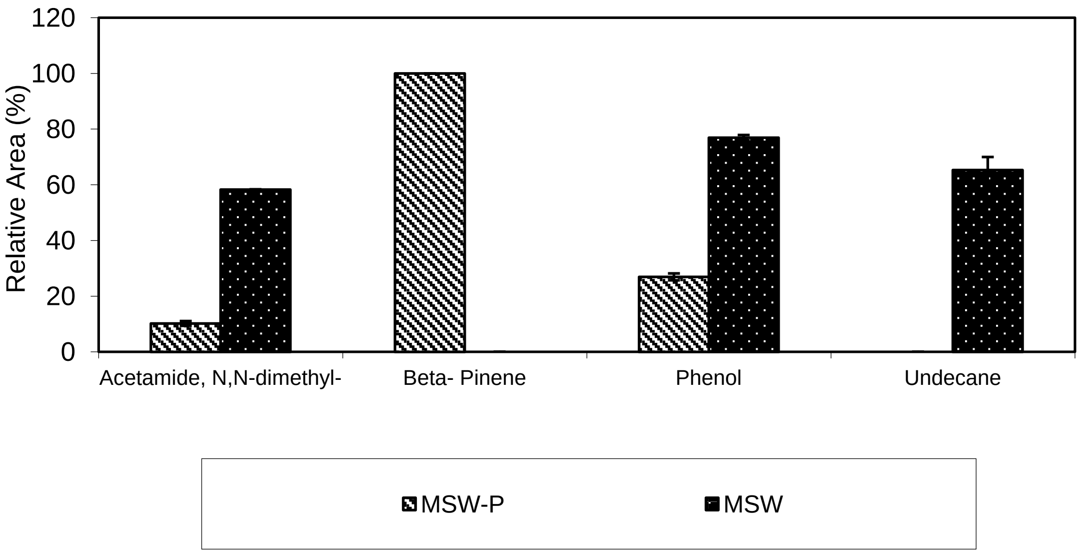

Figure 5.6. Majority volatile organic compounds found in the biofilters by GC/MS at day 0 of the experiment

To avoid this interference, the next analysis was carried out by injecting 0.5 ml of the gas (under investigation or in question) directly into the GC/MS. The chromatograms in Fig.5.7. show the analysis of the gas samples taken from all the sampling ports during day 266 of the experiment. The associated concentrations of α-pinene determined by the VOC detector from all samples were 17.6 ppm$_v$ in the inlet stream, 0.0 ppm$_v$ in the Bio1 output and 10.4 ppm$_v$ in Bio2 output, respectively. These results clearly indicate that the main and more representative compound was α-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 Bio1, while beta-pinene seemed to be only prominent in Bio2. 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.

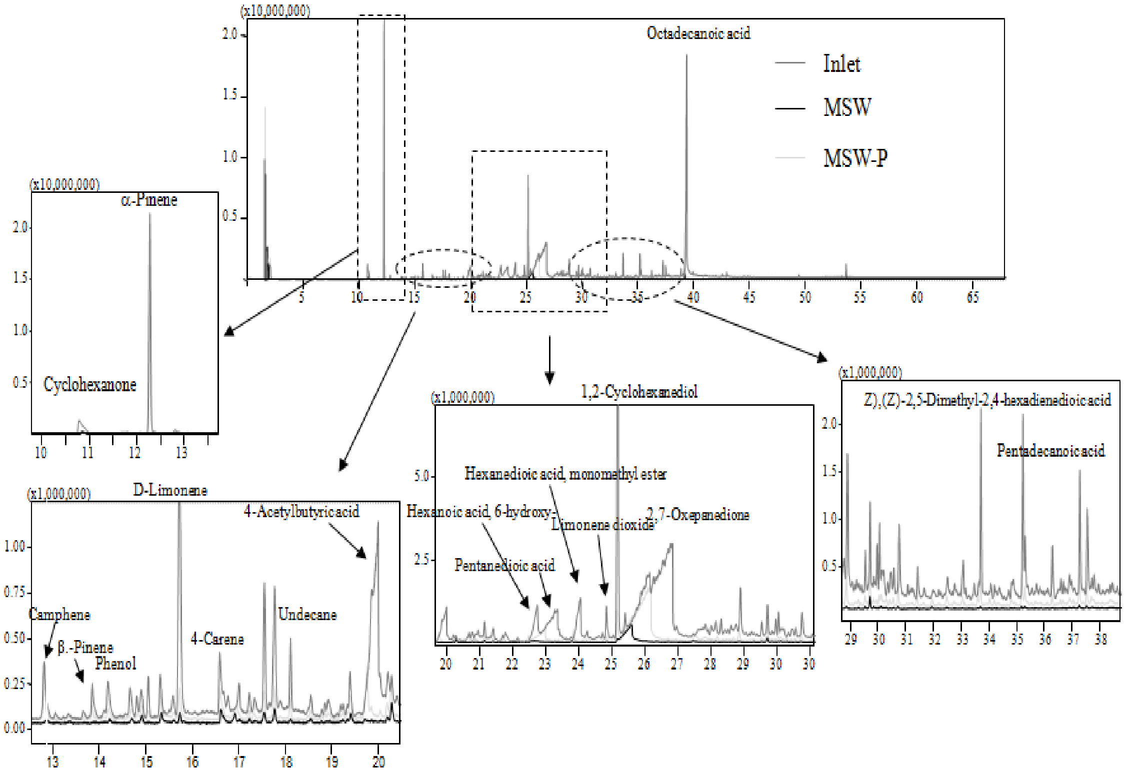

Figure 5.7. Chromatograms obtained by GC/MS of gas samples of the inlet stream and the outputs of the biofilters at day 266

The high removal efficiency reported by the VOC´s detector was consistent with the results from the GC/MS analysis. The α-pinene signal in the chromatograms (Fig. 5.7.) disappears completely if it is compared to the input stream and the

MSW biofilter samples. Table 5.3 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 Bio1 samples. Moreover, the average efficiency of Bio2 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 α-pinene in the biofiltration system.

Table 3. Concentration of the main volatile organic compounds found on day 266 in the different sampling ports using GC/MS (average ± standard deviation[a])

		Inlet	*MSW*[b]	*MSW-P*[b]
α-Pinene	μg l_{air}^{-1}	1969±184	---	1205±114
β-Pinene		16±1	---	20.8±0.51
3-Carene		16.0±0.5	---	3.04±0.18
D-Limonene		103±3	---	13.7±2.1
Undecane		13.5±1.8	---	---

[a] Average ± standard deviation, over four samples, (d.w.)

[b] MSW: Municipal solid waste composts; MSW-P: Municipal solid waste – Pruning residues composts

Fig. 5.8. 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 α-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 Bio1 and 99.2 % in Bio2. 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. Bio1 and Bio2 groups were mainly separated along the χ 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 (López et al., 2011; Sironi et al., 2007) reported similar results using different composts as packing materials and composting processes.

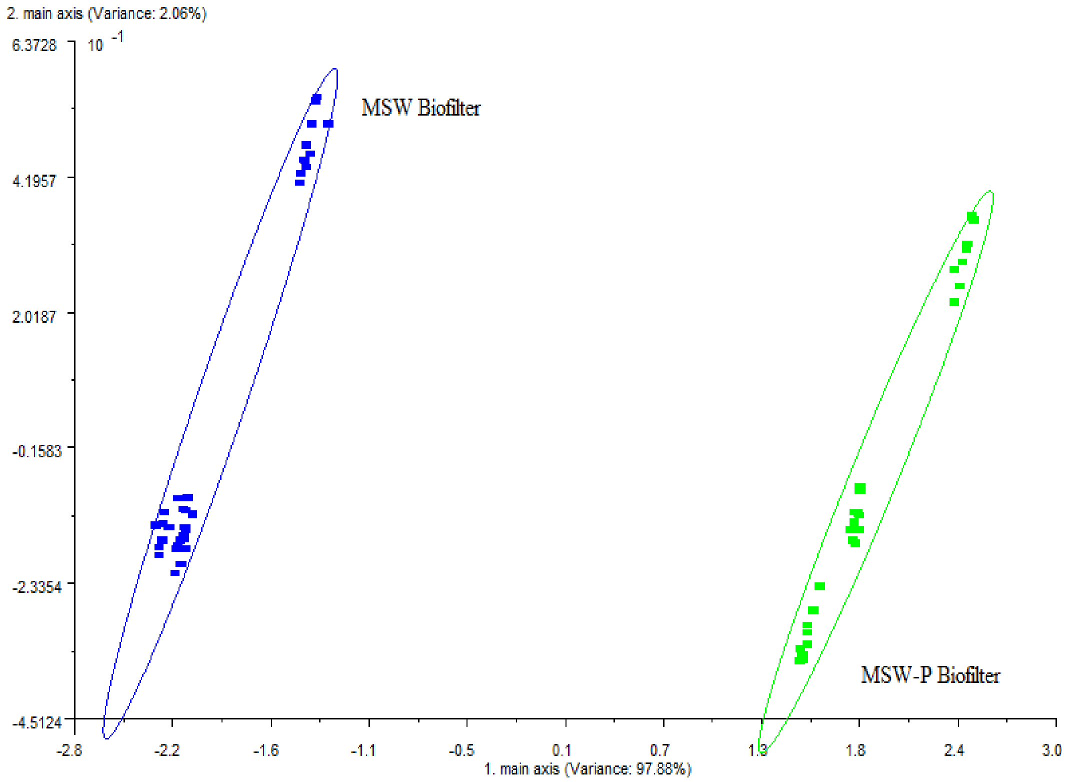

Figure 5.8. Principal Component analysis plots considering MSW Biofilter and MSW-P Biofilter as the classes in samples corresponding to day 88 of the experiment

When the PCA was performed using the sampling ports as the classes, the differentiation between groups was also evident. Fig. 5.9. 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.w) for Bio1 and 43.5 % (d.w) for Bio2, respectively. The removal efficiency values were similar to those found during the GC/MS analysis (98 % Bio1 and 45 % Bio2). The low removal efficiency found in Bio2 is most likely due to the low moisture content of this material. The inlet concentration of α-pinene was 7.8 ppm_v and the output concentrations were 0.2 ppm_v and 4.3 ppm_v for Bio1 and Bio2, 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 α-pinene. In Fig. 5.9. 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 (W1W) 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≥ 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 α-pinene concentration in the samples. In this sense, the air samples (0 ppm_v) and the input samples (7.8 ppm_v) were clearly separated along the χ axis, representing 98.21 % of the total variance whereas Bio2 and the input samples are poorly separated between them. Based on the loading analysis observed the differentiations along the χ axis was mainly due to the W6S and the W1W sensors, this indicates that these sensors, related with breath gases, terpenes and smell gases are the cause of the discrimination power obtained. Furthermore, the differences 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.

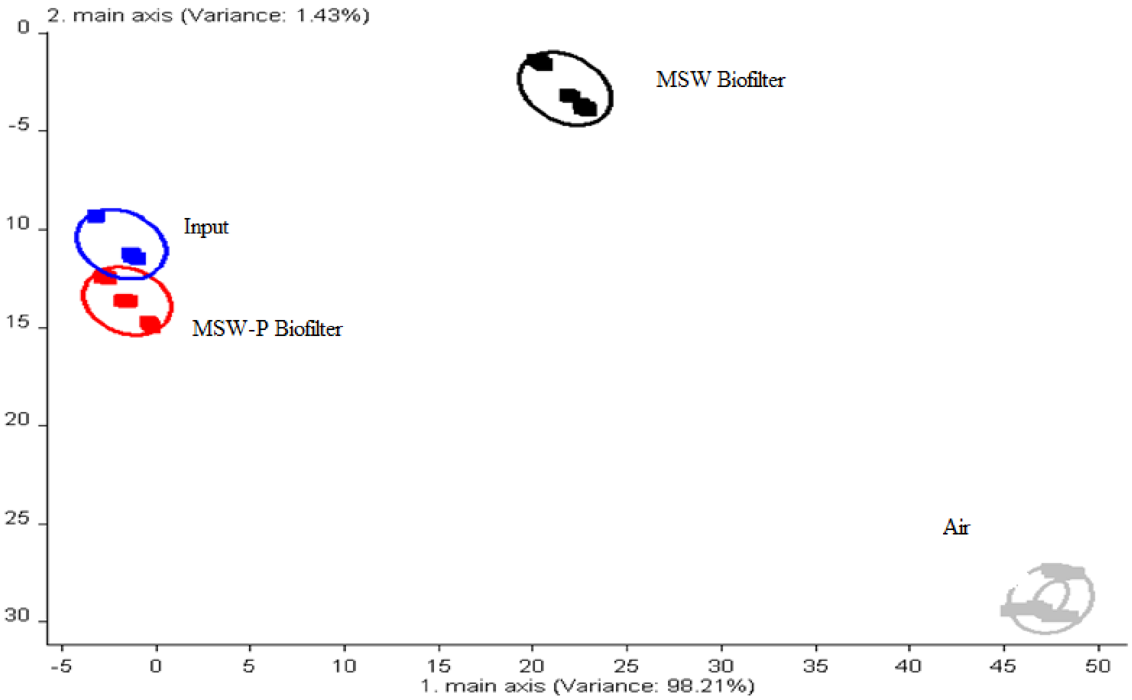

Figure 5.9. Principal Component Analysis plots considering all the sampling ports and air as the classes in samples corresponding to day 223 of the experiment

5.4. CONCLUSIONS

Despite the hydrophobic properties of the contaminant (α- pinene), its moisture content greatly affected the removal efficiency of a biofiltration system using different compost as packing materials. The acclimatization period necessary to reach high removal efficiency was relatively high (10 days for Bio1 and 25 days for Bio2), especially when considering that the materials had previously been used to treat gases containing α-pinene.

The optimal range of moisture content for the packing materials used in this experiment was between 66 and 112 % (d.w) in the case of Bio1 and between 51 and 100 % (d.w) in Bio2. Bio2 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 acclimatization period seemed to be longer for both packing materials.

The GC/MS data support the results obtained with the VOC detector in terms of α-pinene removal efficiencies and did not detect any compound related to a partial degradation of the α-pinene in the biofiltration system. The e-nose could classify the signal emitted by the biofilters when the α-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 α-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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6. TREATMENT OF GASES CONTAMINATED WITH METHYL ETHYL KETONE (MEK) BY BIOFILTERS PACKED WITH MUNICIPAL SOLID WASTE – PRUNING RESIDUES COMPOSTS: PERFORMANCE ASSESSMENT

6.1. INTRODUCTION

2- Butanone or methyl ethyl ketone (MEK) is a widely used industrial chemical. It is a common solvent used for lacquers, adhesives, surface coatings and cleaning materials prior to electroplating (Cai et al., 2004). It is also utilized in making adhesives, printing inks, degreasing, antioxidants, perfumes, magnetic tapes and in conjunction with acetone in the effluent streams from the manufacturing of semiconductors and optics-electronics (ACS, 2003; Chan & Lai, 2010). Because of its extensive use, the US Environmental Protection Agency (EPA) regulates MEK as a volatile organic compound (VOC), which is considered a precursor to ground-level ozone or smog. Thus, industrial releases or transfers of MEK must be reported under EPA’s yearly Toxic Release Inventory (ACS, 2003).

On the other hand, the MEK is the most important compound belonging to the group of ketones emitted during active composting of municipal solid wastes (MSW) - green residues and is considered one of the main odour causing compounds produced during this aerobic treatment (Delgado-Rodríguez et al., 2011). Several authors detected MEK among others ketones during the characterisation of composting and MSW landfill emissions (Davoli et al., 2003; Eitzer, 1995; Kissel et al., 1992; Kumar et al., 2011; Schlegelmilch et al., 2005a;

Tsai et al., 2008). Mao et al. (2006) indentified the MEK as a critical component of odors in food waste composting plants. In the same way, Rajamäki et al. (2005) found that MEK was a suitable indicator compound of anaerobicity during composting experiments using kitchen waste and a bulking agent as raw materials. Among the effects to the exposition of humans to high concentrations of MEK have been reported irritations to the eyes, nose and throat. Nevertheless, limited information is available on the chronic effects of this volatile organic compound in humans from inhalation exposure (EPA, 2000). Although, the reported concentration of MEK emissions by this kind of processes are below the threshold limit value (590 mg/m^3) (Eitzer, 1995). It is clear that MEK is an important component of the nuisance generated by the odours emissions produced during the treatment of residues. The unpleasant odours generated during these processes are one of the main problems associated to composting facilities and anaerobic treatment systems (Delgado-Rodríguez et al., 2010; Müller et al., 2004; Pagans et al., 2005; Ranzato et al., 2012; Tagaris et al., 2003).

The prediction of the potential odor emissions any time a new composting plant is designed is complicated and is considered an important problem (Bidlingmaier & Müsken, 2007). For this reason, the optimization of operation parameters in composting is a concern of the scientific community (Bueno et al., 2009; Delgado-Rodríguez et al., 2011). Nevertheless, the total elimination of the VOCs emissions in this kind of processes is impossible. For this reason, there are different techniques used in the control of VOCs. The most important technologies include physical, chemical and biological processes depending on the physical, thermodynamic and reaction properties of the target compounds as well as the flow rate and the pollutant concentration (Revah & Morgan-Sagastume, 2005; Schlegelmilch et al., 2005b).

The biological processes to remove VOCs from a polluted air stream are considered as highly efficient and have different advantages like low installation and operation/maintenance costs and the absent of secondary residues (Chan & Lai, 2010; Raghuvanshi & Babu, 2009; Xiaobing et al., 2003). The biofiltration technique operates effectively in the treatment of large volumes of waste gas streams containing low concentration of odorous compounds, which corresponds to the characteristics of the biological waste treatment systems (Dorado et al., 2010b; Mudliar et al., 2010). A biofilter is defined as a reactor where is carried out the conversion of different organic and inorganic compounds into harmless oxidation products like water, carbon dioxide and salts (Datta & Grant-Allen, 2005). This process involves the passage of a polluted air stream through a porous packed bed containing microorganisms. The degradation of the contaminants occurs after the transfer of the compounds to the biofilm present in the surface of the material where the microbes will use them as carbon or energy sources (Chan & Peng, 2008). In this way, the mechanisms in biofiltration includes adsortion to the medium and/or adsortion into a water film and finally biodegration of the contaminants within the biofilm (Lebrero et al., 2013; Stoffella & Kahn, 2005). For this reason, the packing materials of the biofilters should be minusciosly chosen. A filter material should have the following properties: High moisture holding capacity, porosity, available nutrients, compression strenghth, and pH buffer capacity (Deshusses et al., 1996). Compost have been widely proposed as bed materials in biofiltration (López et al., 2011; Pagans et al., 2007; Zhu et al., 1998). This material retain moisture for microbial activities and maintain hig air-filled porosities avoiding the clogging of the systems (Mostafid et al., 2012).

Some previous works have evaluated the removal of MEK by biofiltration systems using different packing materials (Cai et al., 2004; Deshusses et al., 1996; Raghuvanshi & Babu, 2009; Xiaobing et al., 2003). Nevertheless, reports evaluating the removal efficiency of biofilters under transient conditions and the influence of the kind of composts used as packing materials in the process are limited.

The industrial biofilters are normally exposed to periods of non-use such as shutdown for factory retooling or equipment repair (Cai et al., 2004). Also, contaminant concentrations in most waste gas streams vary with time due to the unsteady-state nature of industrial processes (Atoche & Moe, 2004). Then, it is necessary the evaluation of this kind of systems under conditions simulating the real situation in order to determine if biofilters are able to maintain a high removal efficiency during changes in operating conditions and interruptions.

Moisture is one of the most critical factors implicated in biofilter effectiveness, because microorganisms require water to carry out their normal metabolic activities. Also, moisture is important for the transport of contaminants to the biofilm and the adsortion processes (Datta & Grant-Allen, 2005; Miller & Allen, 2005). As this transport is ruled by the Henry´s law, the solubility of the VOC in water is a limiting factor. There are several references related with the study of the moisture influence on the removal efficiency of hydrophobic volatile organic compounds (Mohseni & Allen, 2000; Paca et al., 2010; Vergara-Fernández et al., 2012). However, the effect of the packing bed moisture content, under transient conditions, on the performance of biofilters designed to treat single hydrophilic compounds have been slightly studied.

The monitoring of the biofiltration processes is carried out using different techniques like gas chromatography in conjuction with mass spectrometry (GC/MS) and olfactometric techniques following the norm UNE EN 13725 (Chen et al., 2008; Dever et al., 2007; Romain et al., 2005; Valor et al., 2004). However, the continuous and in situ determination of the removal efficiency in biofiltration is really complicated and expensive through the methods mentioned before. Alternative techniques to evaluate volatile organic compounds have been explored in previous research; Rajamäki et al. (2005) studied the volatiles emmited by composting using an electronic nose obtaining clear differences between a well and weakly aerated composting bins. Stuetz and Nicolas (2001) and López et al. (2011) evaluated the use of electronic noses for environmental odour detection and compost based biofilters monitoring respectively.

Nevertheless few references of the use of electronic nose use in the assessment of biofiltration processes efficiency have been found. This technique has an important potential (with a previous training) to evaluate and indentify problems during the biological treatment of volatile organic compounds.

Otherwise, photoionization detector (PID) technology have been proposed to obtain useful information of the general concentration of VOCs in gas streams (Hobbs et al., 1995; Karlik et al., 2002; Muñoz et al., 2010; Smith et al., 2007). The main advantages of the VOCs analyser are its portability, accuracy, quick response (< 2 s) time and reliability in the case of a specific VOC gas (López et al., 2011). Then, this technique could be a complementary tool which enhance the use of less used tools like electronic noses.

In this research, MEK, an hydrophilic volatile organic compound (solubility in water 27.5 g/100 mL), was chosen as the contaminant present in the air stream to treat (White, 2009). This study is focused on the removal efficiency evaluation of two kinds of biofilters, using composts of MSW and MSW-Pruning residues as packing materials, to treat an artificial stream of air containing MEK. This evaluation is performed with the support of several analytical techniques like VOC analyser, electronic nose and GC/MS. The assesment of the system is realized simulating real variations (transient-state) in the most important parameters influencing the process like moisture content of the packing material and inlet concentration. In the same way, the influence of the packing material nature on the degradation of this VOC was evaluated.

6.2. MATERIALS AND METHODS

6.2.1. BIOFILTRATION UNIT

The biofiltration system consisted of a pair of biofilters, each using a different type of mature compost as a packing material. One biofilter was filled with compost from MSW and the other one with compost from MSW: Pruning Residues (P) in a volumetric ratio 1:1. Selected physico-chemical characteristics of the packing materials used are shown in Table 6.1.

Table 6.1. Relevant physico-chemical properties [a] of the packing materials used in the biofiltration system (oven dry basis)

		MSW[b]	*MSW-P*[b]
pH (1:5 extract)		6.65 ± 0.2	6.70 ± 0.1
EC (1:5 extract)	mS m^{-1}	5.46 ± 0.3	6.74 ± 0.1
Organic Matter	g kg^{-1}	213 ± 24	708 ± 99
Kjeldahl-N	g kg^{-1}	15.4 ± 0.1	13.1 ± 0.3
C/N ratio		8.02	31.3
Bulk density	g L^{-1}	665 ± 31	327 ± 35

[a] Average ± standard deviation, over four samples, (d.w.)
[b] MSW: Municipal solid waste composts; MSW-P: Municipal solid waste – Pruning residues composts

Additional details about the composting process carried out to obtain the biofilter mediums are given by Delgado-Rodríguez et al. (2010). The particle size was adjusted for both kinds of packing materials, ranging from 7 to 20 mm, to improve removal efficiency and reduce the probability of operating problems (clogging, control of air flux, etc) reported in previous experiments. Previously, the materials employed in this work were used to treat a gas stream composed of a VOC mixture from the active composting of MSW for up to two months (López et al., 2011) and to treat α-pinene vapours in laboratory. Due to this fact and that natural materials were used as bed packing, no inoculation was performed. The initial moisture of the biofilters media was determined by oven drying at 105 ºC. During the course of the experiment the moisture content of the materials was adjusted periodically, depending of the stage of the assay, by the weight difference between the complete biofilter bed to the initial. When the addition of water was necessary, it was added to the top part of the biofilter. Considering the porosity nature of the materials and that the contaminated stream to be treated was fed to the system with a high content of relative humidity, this method allowed the homogeneous distribution of water in the biofilter. As the nature of the materials was different, the moisture content was expressed in dry weight (d.w) to be able to compare both media.

Each biofilter consisted of a PVC column of 11 cm in diameter and 1 m in height. The upper 95 cm (bed volume 9.0 L) of the biofilter was filled with the compost. The inlet gas stream was supplied from the bottom of the column (ascending flow). Pressurized ambience air was obtained using a compressor free of oil products; the air was taken from the surroundings with the purpose to operate continuously and to facilitate the following humidification process of the air. Depending on the stage of the experiment, the main part of the inlet gas was previously humidified to 90-100% relative humidity, by sparging the gas stream through a reservoir filled with water. In order to generate the contaminated airflow, a small fraction of humidified air was previously fed to a sparger, which contained liquid MEK (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 MEK, guaranteeing the concentration of the contaminant fixed during 6 to 8 hours. The average of this concentration during all the stages of the experiment was 20 ppm_v (59 $mg.m^{-3}$) of MEK. A schematic diagram of the biofilter unit is shown in Fig. 6.1.

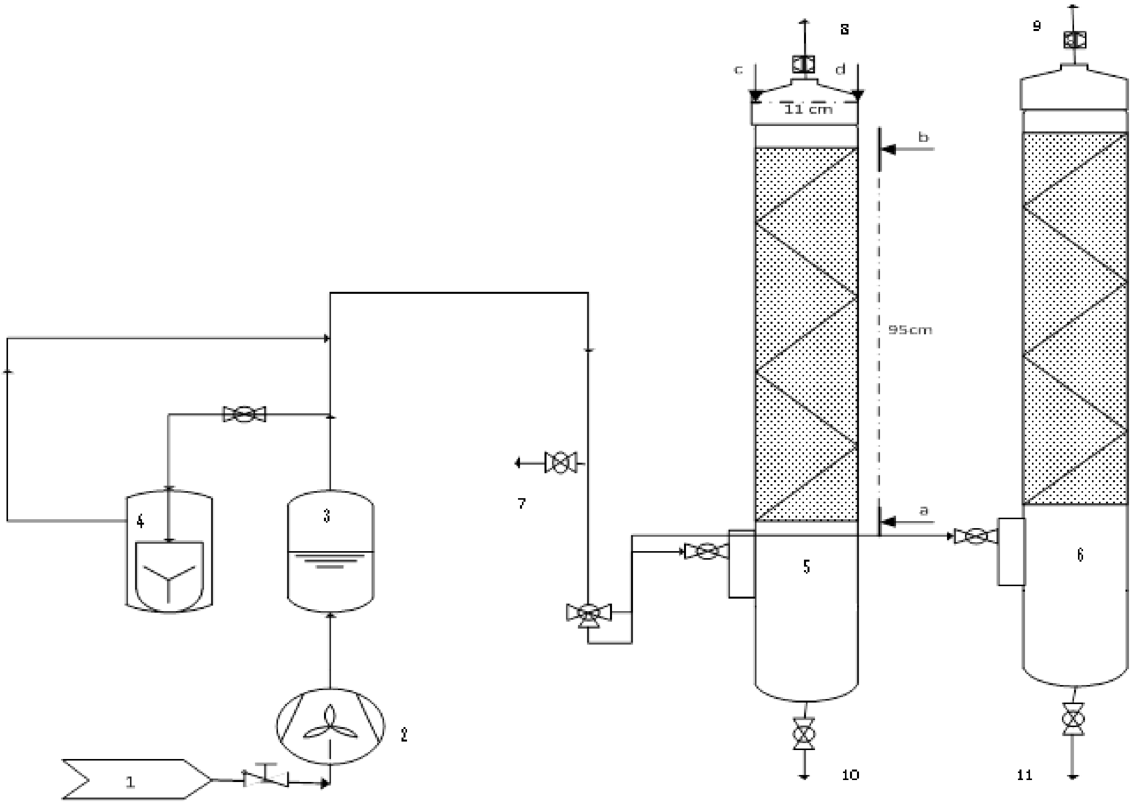

Figure 6.1. Schematic diagram of the biofiltration system. (1) Pressurized air; (2) Compressor; (3) Humidifier; (4) MEK sparger; (5) Biofilter compost MSW; (6) Biofilter compost MSW-P; (7) input sampling port; (8,9) outlet biofilter gas/output sampling port; (10,11) Water drainage

The empty bed residence time (EBRT) was adjusted to 66 s. EBRT values about 1 min were frequent in biofiltration experiments in order to obtain effective degradation in the system (Box & Behnken, 1960; Dorado et al., 2008; López et al., 2011; Omri et al., 2011; Ramírez et al., 2011).

The experiment was separated into different stages, modifying some operative conditions of the system proposed:

Days 1-19: MEK concentrations below 30 ppm_v.

Days 20-211: Increase of the inlet concentration of MEK until a maximum of 2300 ppm$_v$ was reached.

Days 215-292: Decrease of the moisture content of the biofilter media while maintaining constant the MEK concentration (65 ppm$_v$) in the inlet stream to the biofiltration system.

6.2.2. *VOCS ANALYSER MEASUREMENTS*

The rapid and *in situ* measurements of the MEK concentrations in the different sampling ports was carried out using a portable VOCs analyser fitted with a 10.6 eV lamp for photo-ionization (MULTIRAE IR, PGM-54, RAE systems, San José, CA, USA). The sensitivity of the equipment was 0.1 ppm$_v$ in a concentration range up to 200 ppm$_v$. Previous experiments have employed this instrument to obtain semi-quantitative information of the VOCs mixtures emissions with good results (Delgado-Rodríguez et al., 2010; Karlik et al., 2002; Ojala et al., 2006). Having in mind that the unique contaminant present in the streams is MEK, the response of the PID detector is directly proportional to its concentration (RAE_Systems, 2002). The instrument was calibrated with isobuthylene, and then to obtain the MEK concentration a factor of 0.9 was used to multiply the reading (RAE_Systems, 2002).

The sampling gas ports were located immediately before the inlet stream of contaminated air and at the output of each biofilter (Fig.6.1). Gas samples were taken from the lines by means of an internal sampling pump with a flow rate of 0.150 L min^{-1}. The readings were taken during each sampling when signal stabilisation was observed, usually in a time less than 30 s. Each day, three replicate of readings associated to each sampling port were obtained.

This instrument does not detect water but condensation on its UV lamp could provoke variations in the signal obtained (Ojala et al., 2006). With the purpose of avoiding this problem, sampling lines were kept to a minimum and a teflon filter (0.2 µm pore size) was used as a water and particulate material trap.

The removal efficiency was determined as presented in the following equation (Eq.1):

$$RE = \frac{(C_{in} - C_{out})*100}{C_{in}} \quad \text{(Eq. 6.1)}$$

Where, RE: removal efficiency (%); C_{in} : Inlet MEK concentration (ppmv); C_{out}: Outlet MEK concentration (ppmv).

One-way ANOVA and Tuckey's HSD test were used for analysis of the variance and comparison of means. Biofilter type was considered as the independent variable and removal efficiencies as the dependent ones. A p value lesser than 0.05 was selected. The procedures were executed with the statistical software SPSS 15.0 for windows (SPSS Inc.).

6.2.3. ELECTRONIC NOSE ANALYSIS

A commercial combination of chemical sensors and software for the recognition of the pattern signs or odour fingerprint of the gaseous samples, called an electronic nose, was used as a monitoring instrument for the biofiltration system. In this work, PEN3 e-nose (Portable Electronic Nose, Airsense Analytics GmbH, Hagenover, Schwerin, Germany) was employed. The e-nose has an array of 10 different metal oxide sensors (MOS) positioned inside a small chamber (1.8 mL). The analytical system has a special integrated sampling system which by an automatic control (autoranging) prevents overloading of the sensors, and also leads to better and faster qualitative and quantitative analysis.

The measurements with the e-nose were performed directly in the sampling ports configured within the biofiltration system, the same method as measurements were taken with the VOCs analyser. Each measurement was made three times to obtain enough replicates, as well as readings of the ambient air (blank) near to the feed-in point of the compressor used in the experiment.

The time necessary to achieve signal stabilisation was about 60 s for the total range of MEK concentrations. However the set of data selected for the statistical analysis only corresponded to 50 to 60 s (the final 10 s) of the sampling time. Also, a time of 60 s was used as purging time between consecutive measurements. For the e-nose the samples were collected at day 60, 85 and 159 of experimentation.

The large data sets taken by the e-nose were elaborated through statistical multivariate methods such as principal component analysis (PCA) for data reduction. 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 a two dimensional figure, 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-nose built-in software (WinMuster_1.6.2.14, 2010).

6.2.4. *GC/MS ANALYSIS*

The sampling for the chromatographic analysis was performed during the day 167 of the experiment. The samples were taken in the input sampling port and in the output ports of the MSW and MSW-P biofilter, using tedlar bags with a capacity of 3 litres, and GC analysis were performed in less than 24 hours. Samples were stored in darkness at room temperature.

The gas samples were analysed injecting directly, with a gas syringe, 0.5 ml in the instrument. In the case of saturation of the detector, dilution of the sample was required. The inlet samples have a dilution factor of 40 and the volume of injection was 0.2 ml. The desorbed volatile compounds were performed using a gas chromatograph- mass spectrometric (GC-MS) Shimadzu GCMS-QP2010SE (Shimadzu Corporation, Kyoto, Japan) using the parameters indicated in Table 6.2.

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

Type	Shimadzu GCMS-QP2010SE		
Injecting port	Split less		
Injector temperature	250 ºC		
Detector temperature	230 ºC		
Capillary column	HP-5MS (Agilent) 30m x 0.25 mm i.d. x 0.25µm		
Column linear velocity	36 cm/sec. (1 mL/min)		
Oven Program			
Initial temperature	35 ºC		
Initial time	5 min		
	Rate (ºC/min)	Final temp (ºC)	Final time (min)
	5	270	20
Mass Spectrometer			
EI voltage	70 eV		
Mass range, scan mode	m/z 30-550 amu		
Solvent delay	0 min		

6.3. *RESULTS AND DISCUSSION*

In the Fig. 6.2 is represented the daily tendency of the VOC detector signal during the different stages of the experiment. As is reflected, the concentration in the inlet stream was maintained constant during 5 to 10 hours; this was adjusted with the sparging setup of the biofiltration system. In this case, the maximum concentration reached was 21 ppm$_v$ corresponding to the start-up phase of the experiment. In order to create comparable results, the monitoring in the system was performed during the time period at which the VOC's reading was stabilized.

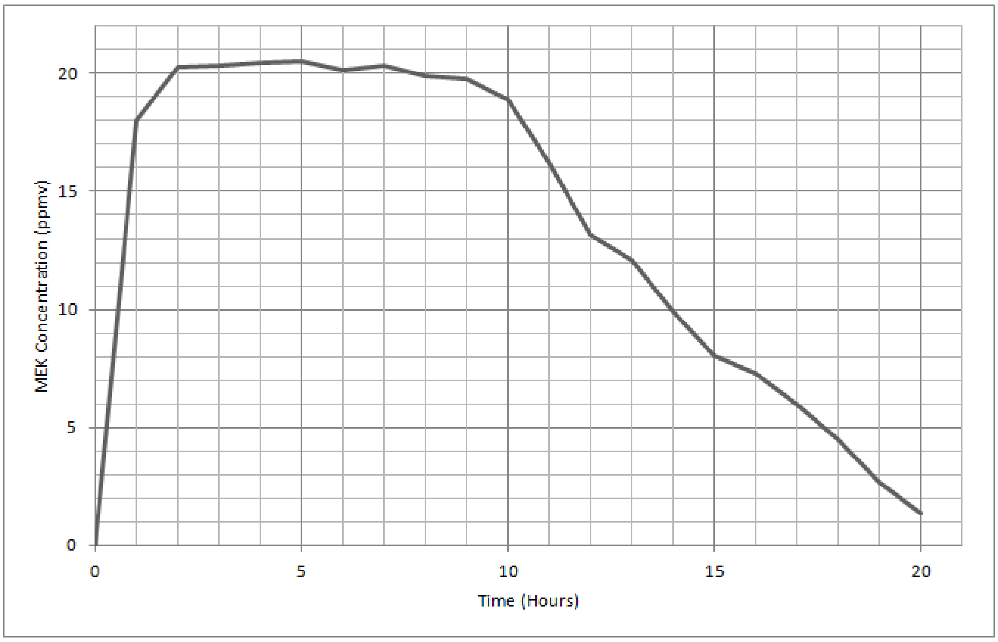

Figure 6.2. Daily evolution of the MEK concentration in the inlet stream during the acclimation phase of the biofiltration system

During the first stage of the experiment (0 to 19 days) the acclimation phase took place (Fig. 6.3).

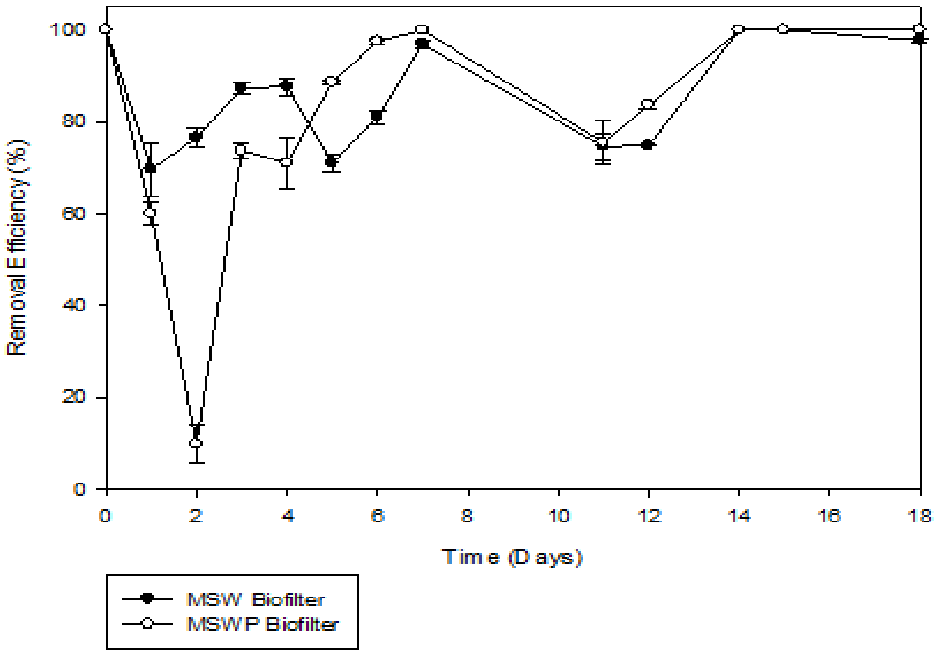

Figure 6.3. Removal efficiency (%) during the acclimation period of the biofilters

MSW biofilter as well as MSW-P biofiler needed approximately 14 days to reach MEK removal efficiencies values near 100% . The moisture content of the materials during this stage was 67.6 % (dw) and 91.8 % (dw) for MSW and MSW-P biofilters respectively. These acclimation periods are within the range of 6 to 40 days reported by previous studies where the biofiltration of MEK was the target (Atoche & Moe, 2004); Chan and Lai (2010) reported a period of 6 days to achieve removal efficiencies near to 100% during the biodegradation of ketones mixtures in a biofilter. Raghuvanshi and Babu (2009) reported acclimation periods of 20 days for biofilters packed with compost and coal. By the other hand, Mathur and Majumder (2008) obtained removal efficiencies of 99.5 % after 40 days during the evaluation of a biotrickling filter to treat a paint solvent mixture which includes MEK. Several authors state that inoculation of the packing materials with adapted microbial aggregates greatly reduces the acclimation time of biofilters (Sercu et al., 2005). In this case, the biofilter media used in this experiment had been used before to treat exhaust gases coming from kitchen waste and pruning residues composting and a gas stream containing α-pinene as contaminant (López et al., 2011), which suggest that the microbial community present in the packing material was adapted to MEK allowing to reach high removal efficiencies in relatively short time (Pagans et al., 2005) and for this reason the direct inoculation of materials used to built the system was not performed. As is shown in Fig. 6.3, a fast increment in the removal efficiency of the system until a value of 80 % occurred in a few days (3-4 days), possibly due to the previous use of the materials mentioned above. Nevertheless, the maximum elimination capacity of the biofilters was obtained after the acclimation time of 14 days, once the microbial community was established and the specific adaptation to the MEK occurred.

The second experimental stage (days 20-211) is shown in the Fig. 6.4, in this case, the MEK concentration in the inlet gas stream was progressively increased to a maximum of 2300 ppm_V.

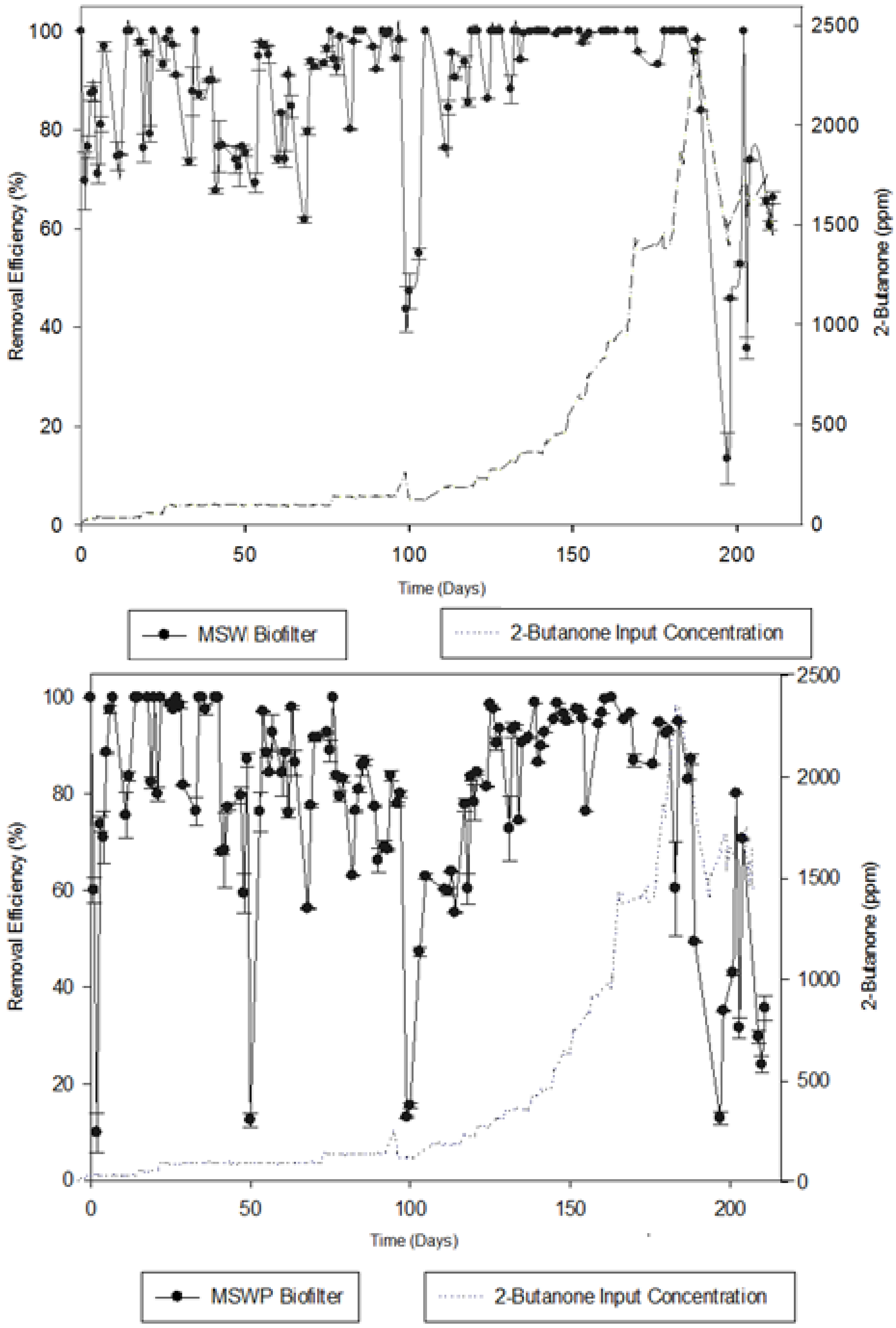

Figure 6.4. Removal efficiency (%) and inlet concentration (ppm$_v$) of MEK in the biofiltration system during the first 211 days of the experiment

It is important to remark that the system presented removal efficiencies near to 100% during the daily first two hours of the experiment, over all the stages of the assay. A similar behaviour was observed during all day 0 of the experiment (Fig. 6.3). For this reason the monitoring activities were performed after two hours from the stabilization of the inlet concentration signal showed in the Fig. 6.2. This phenomenon is attributed to the adsorption and absorption processes occurred in the biofilters. Biofiltration is usually described as an initial step of adsorption followed by biodegradation. Nevertheless, previous works have demonstrated that absorption must be considered as an important mechanism of pollutant removal in biofiltration, especially when hydrophilic pollutants are treated using organic complex materials (Pagans et al., 2007). Then, the fluctuations observed in the performance of the biofilters (Fig. 6.4) could be attributed to different process occurring during the degradation of MEK. The abrupt decrease of the MSW-P biofilter removal efficiency observed in Fig. 6.3 during the day 50 coincided with a scheduled shutdown of the system (day 49) with the purpose to evaluate the adsorption/absorption phenomena during the biodegradation of MEK. The removal efficiencies obtained during day 50 were 75.3 % and 12.4 % for MSW and MSW-P biofilters respectively. These values indicate that MSW biofilter practically was not affected by the non-operational period possibly due to the nature of the contaminant which its origin is more related with this packing material than the MSW-P biofilter (Bagherpour et al., 2005). On the other hand, despite the adsorption capacities of organic materials like the media used in MSW-P biofilter that suggest the material’s suitability as a buffer to smooth intermittent pollutant loads or non-operational periods (Dorado et al., 2010a); this biofilter required a re-acclimation period after the scheduled shutdown.

The removal efficiency of the MSW biofilter became unstable starting to decrease to values below 90 % as MEK concentration was increased over 2200 ppm_v (day 187). In the same way, MSW-P biofilter removal efficiency showed a sharper decrease followed by a progressive recovery when the inlet concentration was 190 ppm_v (day 100). However, the performance was affected again when the inlet concentration was set up at 2200 ppm_v as well as the MSW biofilter.

The abrupt decrease of the removal efficiency in both biofilters occurred at day 100 was resulted from a sudden change in the MEK concentration of the inlet stream (Fig. 6.4). The same effect was observed immediately after several non-operational days of the system. These temporary efficiency reductions would indicate that the biofilters needed a re-acclimation time (Kleinheinz et al., 1999) every time any change was made.

After a sharp decline of the efficiency in the system occurred on day 197 (Fig. 6.4), the concentration in the inlet stream was fixed to values around 1500 - 1600 ppmv, with the purpose to evaluate the capacity of stabilisation by the system when the contaminant concentration was reduced. Nevertheless, after 14 days the fluctuation in the system was evident tending to a new equilibrium with values of removal efficiencies below the maximum reached in other stages of the experiment. Then, at the end of this stage, when the concentration of the compound in the inlet gas stream was 1536 ppmv, the average efficiency was 66.2 % and 35.6 % in MSW and MSW-P biofilter, respectively. These figures corresponded to an elimination capacity of MEK by the system of 151.6 $g.m^{-3}$

bed media.h^{-1} (MSW biofilter) and 70.4 g.m^{-3} bed media.h^{-1} (MSW-P biofilter). Deshusses and Hamer (1993) obtained a maximum elimination capacity (EC) of 50 g.m^{-3} bed media.h^{-1} using biofilters with an inlet MEK concentration of 101 ppmv. In the same way, Chan and Lai (2010) reported a maximum EC of 59.9 g.m^{-3} bed media.h^{-1} during the treatment of ketone mixtures with MEK concentrations in the range of 50-300 ppmv using PVA/peat/GAC/KNO_3 composite beads biofilters. During the studies of removal of MEK using biofiltration carried out by Raghuvanshi and Babu (2009) the results of the shock loading phase revealed elimination capacities of 168 to 174 g.m^{-3} bed media.h^{-1} with inlet concentrations in the range of 407 – 417 ppm_v; The packing material used in this case was a mixture of mature compost and coal in the ratio of 2:1 (v/v) and an EBRT of 20.6 s.

However, no previous studies have reported inlet MEK concentration that are greater than or equal to 1470 ppm_v which corresponds to a medium removal efficiency of 95 %, suggesting that the proposed biofiltration system would enlarge the range of working concentrations.

In the Fig. 6.5 is showed a Tuckey's HSD test ($p < 0.05$) comparing the weekly removal efficiencies of the two biofilters evaluated. The data analysed corresponded to the first and second stage of the experiment. The values of removal efficiency in the same week followed by the same letter are not statistically different. With exception of the period from week 19 to week 26 which coincides with the increment of the inlet concentration until its maximum value, the nature of the packing materials presented significant differences in terms of MEK removal efficiency during all the stages of the assay.

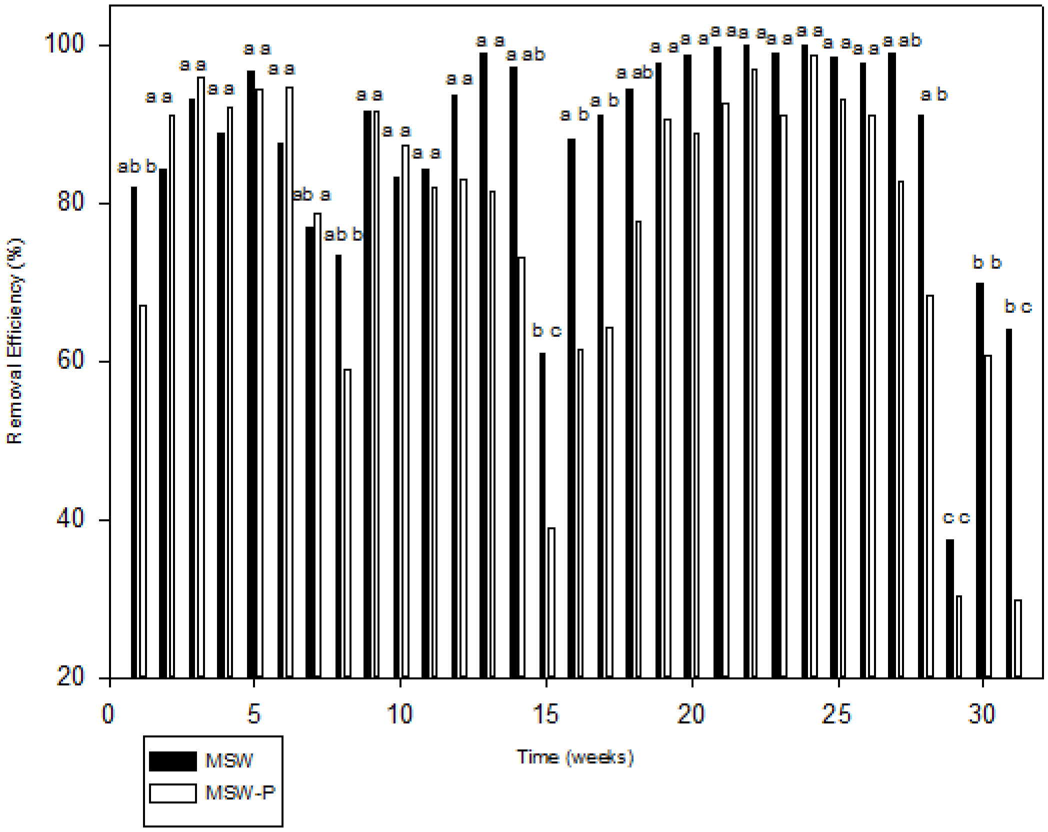

Figure 6.5. Tuckey's HSD test ($p < 0.05$) comparing the weekly removal efficiencies of the two biofilters evaluated (values of removal efficiency in the same week followed by the same letter are not statistically different)

In the third phase of the experiment, from day 215 to day 292 (Fig. 6.6), the moisture content of the packing materials was reduced progressively by eliminating the humidification unit. The inlet MEK concentration was set at 65 ppm$_{v,}$ based on the results obtained from the previous stages, where removal efficiency was highest (at this concentration). At this phase, the study aimed to observe the influence of the moisture content on the performance of the two biofilter systems after a transition phase of 4 days used for re-acclimation. After this period, when the moisture content was 67.5 % (d.w) and 91.8 % (d.w) for the MSW and MSW-P biofilter respectively, the removal efficiency for both biofilters was 100 % (Fig. 6.6).

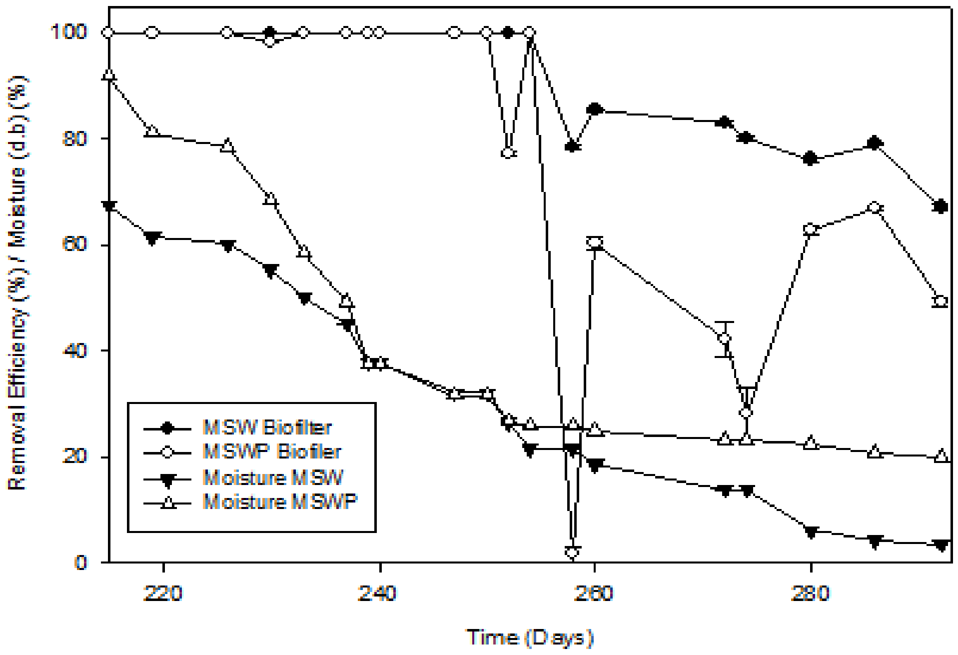

Figure 6.6. Biofiltration system performance during the decrease of the moisture content of the packing materials

The biofilter performance however was adversely affected when the moisture content of the packing materials was set below 21.5 % for MSW biofilter and 25.7 % for MSW-P biofilter with removal efficiencies observed to be lower than 80 %.

These results indicated that the optimum moisture content range for the packing materials and the EBRT used in this experiment was between 21.5 and 67.5 % (d.w) in the case of the MSW biofilter and between 25.7 and 91.8 % (d.w) for MSW-P biofilter, respectively. Krailas et al. (2000) found that when the water content in the compost was below 35 % (d.w) microbial activity was impaired affecting the elimination capacity of a hydrophilic contaminant by the system. It is important to remark that once the compost media had dried, it became hydrophobic and could be rewetted only with great difficulty (Sun et al., 2002). In this case, the initial moisture content was readjusted with the purpose to observe the adaption capacity of the system. Once the moisture content was fixed in the range of optimum values, the removal efficiency in both biofilters was recovered.

Fig. 6.7 shows the results obtained during the monitoring of the system on day 167 by GC/MS.

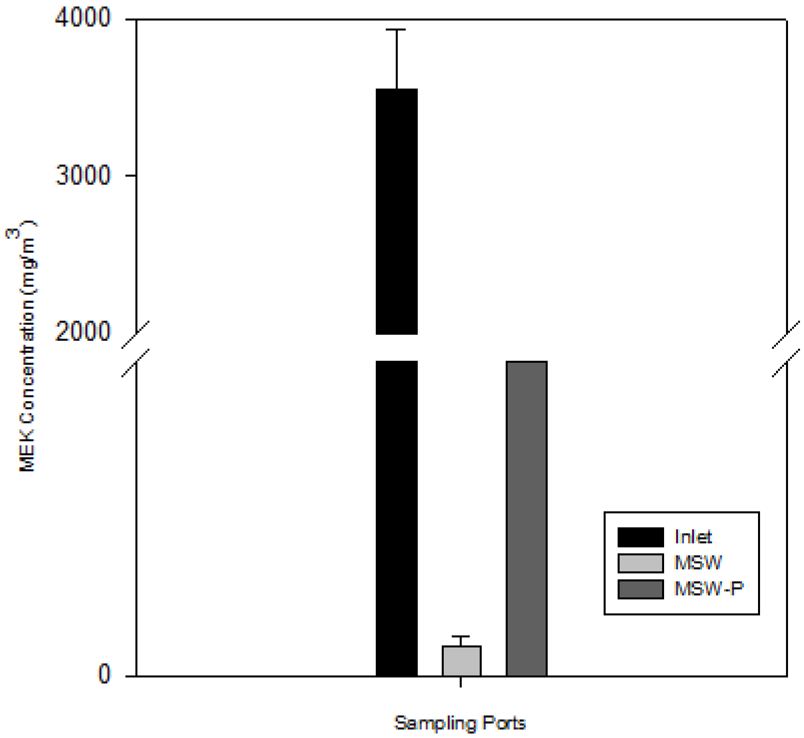

Figure 6.7. Quantification of the MEK concentration in the different sampling ports during the monitoring of the system on day 167 by GC/MS.

The associated concentrations of MEK determined by the VOC detector from all samples were 2940.7 mg.m^{-3} in the inlet stream, 0.0 mg.m^{-3} in the MSW biofilter output and 148.7 mg.m^{-3} in the MSW-P biofilter output. The high removal efficiency reported by the VOC´s detector was consistent with the results from the GC/MS analysis. The removal efficiencies obtained by GC/MS are 99.8 % and 91.3 % for MSW and MSW-P biofilter respectively.

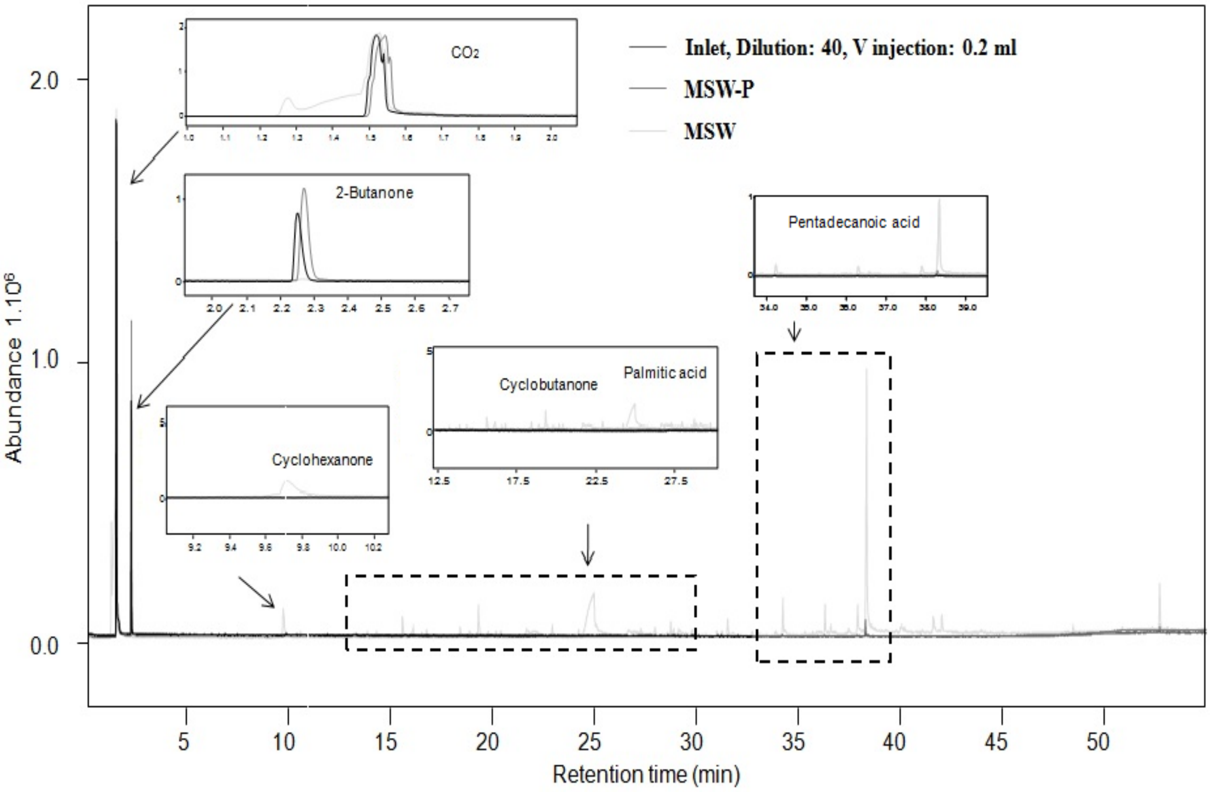

Figure 6.8. Chromatograms obtained by GC/MS of gas samples of the inlet stream and the outputs of the biofilters at day 167

The chromatograms in Fig.6.8 show the analysis of the gas samples taken from all the sampling ports during day 167 of the experiment. These results clearly indicate that the main and more representative compound was the MEK. However, there were other VOCs present in the chromatograms, which could be impurities of the reactive or natural compounds in the surrounding air. These compounds were pentadecanoic acid, palmitic acid, cyclobutanone and cyclohexanone, found in samples corresponding to the MSW biofilter and the inlet stream principally (having in mind that the signal corresponding to this stream is diluted, Pentadecanoic acid). It is important to remark that these compounds were reported as emitted during MSW composting (Delgado-Rodríguez et al., 2012). Then, the presence of some of these VOCs could be part of the natural fingerprint of the packing material used in the MSW biofilter.

In the same way, the MEK signal in the chromatograms (Fig. 6.8) disappears completely if it is compared to the inlet stream and the MSW biofilter samples. Moreover, GC/MS analysis did not found any compound related to a partial degradation of the MEK in the biofiltration system.

Fig. 6.9 presents the PCA carried out using the response of 4 metal oxide sensors without include the dilution factor of the e-nose used in the experiment on days 60, 85 and 159 of the experiment respectively. These diagrams represent different conditions of the system during the performance of the assay. The conditions of the samples used to perform the multivariate analysis are shown in Table 6.3. 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. As is shown in the Fig. 6.9 the media associated variance of the two principal components in PCA was 99.75 %, which means that the system was represented correctly by these two new uncorrelated variables. In all cases the multivariate analysis was performed using the sampling ports and the surrounding air as the classes and all groups were mainly separated along the χ axis (Function 1), which accounted over 95 % of the total variance. 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; despite in some cases (Fig.

6.9a) the concentration of MEK in the output stream of both biofilters was similar. Previous studies (López et al., 2011; Sironi et al., 2007) reported similar results using different composts as packing materials and composting processes.

Table 3. Characterization of the samples used in the multivariate analysis (PCA)[a] and removal efficiency (RE) of each biofilter

Day	*[ ] Inlet*	*[ ]MSW (ppm$_v$)*	*[ ]MSW-P (ppm$_v$)*	*RE MSW[b]*	*RE MSW-P[b]*
60	93.9±1.4	27.1±0.8	16.3±9	74±1.2	84.4±8.4
85	141.6±0.5	0	22.1±5.7	100	85.9±3.6
159	826.7±1.3	0	49.9±0.1	100	94.5±0.1

[a] Average ± standard deviation, over four samples
[b] MSW: Municipal solid waste biofilter; MSW-P: Municipal solid waste – Pruning residues biofilter

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 MEK. In Fig. 6.9 is shown this representation where the sensors included in the analysis were (i) hydrogen (W6S), which is selective to hydrogen and breath gases, (ii) aromatic (W3C) that is reported to be sensitive to aromatic compounds, (iii) the methane-aliphatic sensor (W3S) that is reported react to high concentrations ≥ 100 ppm and sometimes is very selective to methane and other aliphatic compounds and (iv) the aromatic sensor (W1C) sensitive as well to aromatic compounds which its reference is the toluene. The PCA shows a clear differentiation of all the studied classes and seems to be a function of the MEK concentration in the samples. In fact in all cases is easy to extract conclusions about the performance of each biofilter based on the PCA diagrams through a comparison with the other classes represented (air and inlet stream), determining which one has a better degradation of MEK in terms of the removal efficiency. In this sense, for example, during day 85 (Fig. 6.9b) the MSW-P biofilter has a lower elimination capacity of MEK compared with the MSW biofilter demonstrated by the lower separation of the first samples along the χ axis (representing the 98.62 % of the total variance) with respect to the inlet samples, whereas the MSW biofilter and the inlet samples are more separated between them.

In the same way, in the day 159 of experimentation, when the removal efficiencies of both biofilters were over 90% (Fig 6.9c), the differentiation of the biofilters samples is represented in theƴ axis with a variance of 0.92 % of the total. Moreover, the biofilter classes are highly separated from the inlet class and scarcely separated from the surrounding air class along the χ axis (representing the 98.15 % of the total variance), which suggests that both biofilters have a concentration of MEK different from the inlet stream and samples are more related with clean air samples.

Based on the parallel loading analysis, in all the diagrams the differentiations along the χ axis was mainly due to the W6S and the W3S sensors, this indicates that these sensors, related with breath gases, high concentrations of volatile organic compounds ≥(100 ppm) and some aliphatic compounds (the MEK) are the cause of the discrimination power obtained.

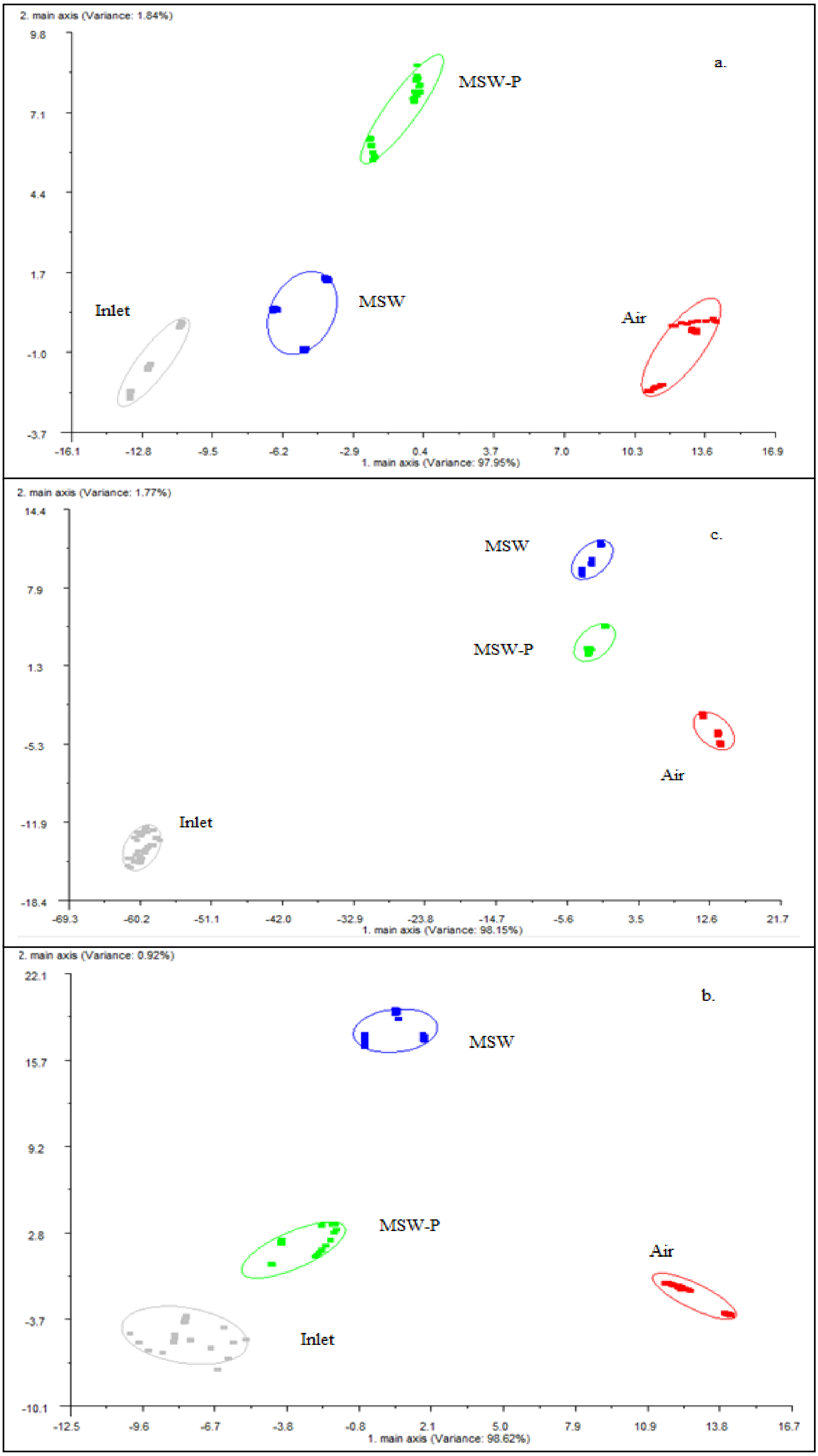
2. main axis (Variance: 1.84%)
9.8
7.1
4.4
1.7
-1.0
-3.7
-16.1
-12.8
-9.5
-6.2
-2.9
0.4
3.7
7.0
10.3
13.6
16.9
1. main axis (Variance: 97.95%)
a.
MSW-P
MSW
Inlet
Air
2. main axis (Variance: 1.77%)
14.4
7.9
1.3
-5.3
-11.9
-18.4
-69.3
-60.2
-51.1
-42.0
-32.9
-23.8
-14.7
-5.6
3.5
12.6
21.7
1. main axis (Variance: 98.15%)
c.
MSW
MSW-P
Air
Inlet
2. main axis (Variance: 0.92%)
22.1
15.7
9.2
2.8
-3.7
-10.1
-12.5
-9.6
-6.7
-3.8
-0.8
2.1
5.0
7.9
10.9
13.8
16.7
1. main axis (Variance: 98.62%)
b.
MSW
MSW-P
Air
Inlet

Figure 6.9. Principal Component Analysis plots considering all the sampling ports and ambient air as the classes. a. Day 60, b. Day 85, c. Day 159

6.4. CONCLUSIONS

The hydrophilic nature of the contaminant (MEK) influences the treatment process of gas streams containing it by a biofiltration system, using different compost as packing materials. The high solubility in water of the volatile organic compound studied promotes the occurrence of different processes during the biofiltration of this contaminant. Despite, biofiltration is usually described as an initial step of adsorption followed by biodegradation. The different fluctuations of the system and the variation of monitoring results during the first hours of the experiment in the same day, suggest that as was reported by Pagans et al. (2007), absorption must be considered as an important mechanism of pollutant removal in biofiltration when hydrophilic pollutants are treated using organic complex materials like in this case.

The acclimation period necessary to reach high removal efficiencies using the packing materials described was 14 days for both biofilters.

The moisture content of the biofilters beds affects the removal efficiencies of MEK. Nevertheless, the influence was less than the expected considering the nature of the contaminant. Then, the optimal range of moisture content for the packing materials used in this experiment was between 21.5 and 67.5 % (d.w) in the case of the MSW biofilter and between 25.7 and 91.8 % (d.w) for MSW-P biofilter, respectively. The lower limit of the range should be treated with caution because although in this case the removal efficiency was not affected, values of moisture content below 35 % (d.w) could impair the microbial activity affecting the future elimination capacity of the contaminant and complicating the re-acclimation periods when planned shutdowns are required.

These results provide important information for the future scaling of biofiltration systems in the industry, where water supply in a biofilter must be optimized.

MSW biofilter showed higher removal efficiency during the different phases of the experiment, possibly due to the natural affinity of this material with the contaminant. Even during the phase where the moisture content of the packing materials was reduced progressively. For both biofilters, after low moisture conditions, the removal efficiency was recovered when the moisture was adjusted in the range described above.

The GC/MS data support the results obtained with the VOC detector in terms of MEK removal efficiencies and did not detect any compound related to a partial degradation of the MEK in the biofiltration system. The e-nose could classify the signal emitted by the biofilters when the MEK concentration was similar, 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 MEK in the streams and to determine the performance of the biofilters when the classes in the multivariate analysis are the inlet, the surrounding air and the outputs of the system. These results suggest further application of the e-nose as an important tool for the monitoring of biofiltration facilities.

Different tools to monitor biofilter operation can be the basis for the implementation of control strategies to sustain long term operation of high performance biofilters.

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7. GENERAL CONCLUSIONS

Both materials (MSW, LTR) evaluated in this study were adequate feedstocks for co-composting.

Time is an important parameter directly influencing the degradation of the materials during the process and affecting the stability of the products.

The results of the modelling suggest that an optimized ratio MSW/LTR of 1/1 (w/w) (equivalent to C/N 60), moisture content in the range of 40-55% and moderate to low aeration rate (0.05-0.175 L_{air} kg^{-1} min^{-1}) is recommended to maximise degradation and to obtain a stable product during co-composting of the described raw materials.

The predicted evolutions and the relations among independent and dependent parameters obtained from the model used are in concordance with the current knowledge of the composting process, showing this model could be effectively applied to the composting process.

The biofiltering process of the pilot composting gases by different MSW or MSW-pruning waste compost reached VOC removal efficiencies greater than 90%.

The e-nose could identify qualitative differences among the biofilter output gases at very low concentration of VOCs related to compost nature and, compost particle size. Sensors detecting sulphur containing-compounds were especially discriminating. The e-nose could also be used to quantify total-VOCs content in air samples during a 20 day composting and biofiltering trial.

Despite the hydrophobic properties of the contaminant (α- pinene), its moisture content greatly affected the removal efficiency of a biofiltration system using different compost as packing materials. The acclimatization period necessary to reach high removal efficiency was relatively high (10 days for Bio1 and 25 days for Bio2), especially when considering that the materials had previously been used to treat gases containing α-pinene.

The optimal range of moisture content for the packing materials used in the α-pinene experiment was between 66 and 112 % (d.w) in the case of Bio1 and between 51 and 100 % (d.w) in Bio2. Bio2 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 acclimatization period seemed to be longer for both packing materials.

The GC/MS data support the results obtained with the VOC detector in terms of α-pinene removal efficiencies and did not detect any compound related to a partial degradation of the α-pinene in the biofiltration system. The e-nose could classify the signal emitted by the biofilters when the α-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 α-pinene in the streams. These results suggest further application of the e-nose as an important tool for the monitoring of biofiltration facilities.

The hydrophilic nature of the contaminant (MEK) influences the treatment process of gas streams containing it by a biofiltration system, using different compost as packing materials. The high solubility in water of the volatile organic compound studied promotes the occurrence of different processes during the biofiltration of this contaminant. Despite, biofiltration is usually described as an initial step of adsorption followed by biodegradation. The different fluctuations of the system and the variation of monitoring results during the first hours of the experiment in the same day, suggest that as was reported by Pagans et al. (2007), absorption must be considered as an important mechanism of pollutant removal in biofiltration when hydrophilic pollutants are treated using organic complex materials like in this case.

The moisture content of the biofilters beds affects the removal efficiencies of MEK. Nevertheless, the influence was less than the expected considering the nature of the contaminant. Then, the optimal range of moisture content for the packing materials used in this experiment was between 21.5 and 67.5 % (d.w) in the case of the MSW biofilter and between 25.7 and 91.8 % (d.w) for MSW-P biofilter, respectively. The lower limit of the range should be treated with caution because although in this case the removal efficiency was not affected, values of moisture content below 35 % (d.w) could impair the microbial activity affecting the future elimination capacity of the contaminant and complicating the re-acclimation periods when planned shutdowns are required.

These results provide important information for the future scaling of biofiltration systems in the industry, where water supply in a biofilter must be optimized.

MSW biofilter showed higher removal efficiency during the different phases of the experiment during the treatment of the stream contaminated with MEK, possibly due to the natural affinity of this material with the contaminant. Even during the phase where the moisture content of the packing materials was reduced progressively. For both biofilters, after low moisture conditions, the removal efficiency was recovered when the moisture was adjusted in the range described above.

The GC/MS data support the results obtained with the VOC detector in terms of MEK removal efficiencies and did not detect any compound related to a partial degradation of the MEK in the biofiltration system. The e-nose could classify the signal emitted by the biofilters when the MEK concentration was similar, 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 MEK in the streams and to determine the performance of the biofilters when the classes in the multivariate analysis are the inlet, the surrounding air and the outputs of the system. These results suggest further application of the e-nose as an important tool for the monitoring of biofiltration facilities.

Different tools to monitor biofilter operation can be the basis for the implementation of control strategies to sustain long term operation of high performance biofilters.