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Development and application of a hybrid inert/organic packing material for the biofiltration of composting off-gases mimics

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ABSTRACT

The performance of three biofilters (BF1–BF3) packed with a new hybrid (inert/organic) packing material that consists of spherical argyle pellets covered with compost was examined in different operational scenarios and compared with a biofilter packed with pine bark (BF4). BF1, BF2 and BF4 were inoculated with an enriched microbial population, while BF3 was inoculated with sludge from a wastewater treatment plant. A gas mixture containing ammonia and six VOCs was fed to the reactors with N-NH_3 loads ranging from 0 to 10 g N/m^3 h and a VOCs load of around 10 g C/m^3 h. A profound analysis of the fate of nitrogen was performed in all four reactors. Results show that the biofilters packed with the hybrid packing material and inoculated with the microbial pre-adapted population (BF1 and BF2) achieved the highest nitrification rates and VOCs removal efficiencies. In BF3, nitratation was inhibited during most of the study, while only slight evidence of nitrification could be observed in BF4. All four reactors were able to treat the VOCs mixture with efficiencies greater than 80% during the entire experimental period, regardless of the inlet ammonia load.

1. Introduction

Since the commencement of intense efforts in biofiltration research in the early eighties, biological techniques for waste gas abatement have proved to be a reliable and economical alternative to traditional physico-chemical technologies in a wide range of operating conditions. However, although their substantial advantages should ideally warrant widespread use, the selection of biological waste gas treatment technologies is still mainly restricted to the treatment of odorous emissions, which tend to contain very low concentrations of pollutants [1]. The main reason for this apparently low implantation is that biofiltration is still considered to be an emerging technology. Successful real-scale biofiltration systems must be durable and economical.

Since the packing material is the main factor influencing both reactor long-term operational stability and global (investment + operating) costs, a packing material should ideally be durable (hence, mechanically and chemically stable and not generating high pressure drop values) and cheap to assure a robust and economical performance. Additionally, it should contain the nutrients required for bacterial metabolism. So far, both organic and inert materials have been used as filter bed in industrial bioreactors. However, the former have a relatively low durability (up to a few years), while the latter tend to be expensive and usually require a periodical nutrient supply. Consequently, the development of a material comprising the advantages of both organic and inorganic materials might lead to an improvement in the performance of biofilters. Lately, new packing materials have been developed focusing on the characteristics which have a greater influence on the performance of the biofilter [2,3].

Besides packing material, the inoculum plays a key role in the efficiency of the bioreactors, especially during start-up [4]. Several studies have demonstrated that a specific inoculation is required for ammonia oxidation [5–7]. Nevertheless, ammonia was removed onto the packing material mainly by absorption. Regarding VOCs abatement, Ortiz et al. proved that the start-up of a perlite packed biofilter treating pentane and inoculated with pre-grown mycelia was faster than with non-adapted inocula [8]. In recent years, several experiments have shown that the removal of pollutants may be enhanced when fungi grow in the reactor [9,10]. Thus, their growth seems to represent an interesting alternative to improve the performance of biofilters treating air contaminated with hydrophobic compounds [11]. Nevertheless, fungal biofilters may have clogging problems due to the growth of filamentous fungi [8]. Therefore, inoculation with a specific pre-enriched microbial culture might slow down the uncontrolled biomass growth and postpone clogging problems, as well as reduce the start-up phase. Although some studies have been carried out comparing the effect of different inoc-

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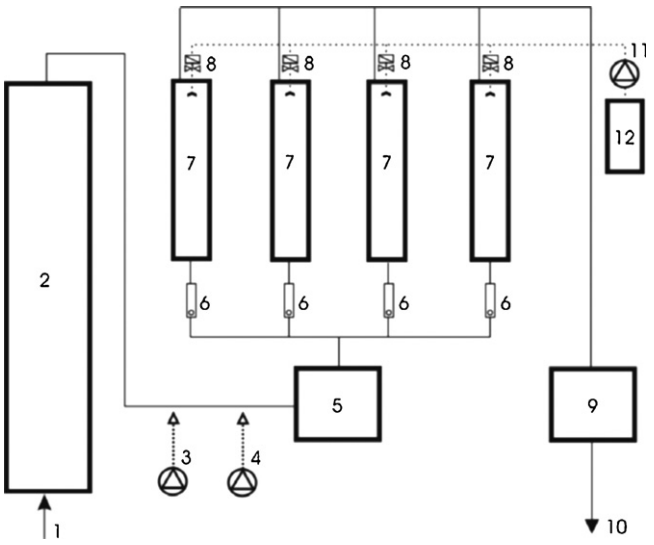

Fig. 1. Schematic of the biofiltration setup. (1): Air inlet; (2): humidification column; (3): peristaltic pump for ammonia supply; (4): microburette for VOCs supply; (5): mixing chamber; (6): rotameters; (7): biofilters; (8): PC-controlled electrovalves; (9): adsorption chamber; (10): air outlet; (11): PC-controlled watering pump; (12): water reservoir.

ula on pollutant removal efficiency [4,8,9], there is still a lack of studies comparing different inocula in bioreactors treating a wide mixture of pollutants.

The aim of this work is to compare the performance of a new, hybrid packing material versus a classical packing material such as pine bark and to assess the impact of using growing enriched cultures as inocula on ammonia and VOCs biodegradation. Thus, an adapted microbial culture was prepared in order to serve as an inoculum for biofilters treating a mixture of seven pollutants. Hexanal, butyric acid, α-pinene, DMS (dimethyl sulphide), DMDS (dimethyl disulphide), MIBK (methyl isobutyl ketone) and ammonia were the seven pollutants present in the mixture. These compounds were selected as they regularly appear in emissions of municipal solid waste treatment facilities [12]. DMS, DMDS and α-pinene are known to be some of the most significant odorous VOCs at wastewater sludge composting facilities [13].

2. Materials and methods

2.1. Biofiltration plant setup

The work was carried out in a laboratory-scale biofiltration plant (Fig. 1) comprising four PVC conventional biofilters (BF1–BF4) with a height of 70 cm and an internal diameter of 8.6 cm each. Reactors were packed up to a height of 50 cm, resulting in a volume of 2.9 L per biofilter. BF1, BF2 and BF3 were packed with a hybrid, innovative filter bed material that consisted of clay spherical pellets covered with compost. The diameter of the particles was between 3 and 5 mm. On the contrary, BF4 was packed with pine bark.

The setup was fed with compressed dry air. In order to increase the moisture content of the stream, a humidification column was installed in the gas line, upstream from the reactors. The gas pressure and flow rates were set by means of manometers and rotameters, respectively. Pure ammonia was pumped to the main air stream from an 8.1 L Tedlar™ bag by means of a VC-MS/CA8-6 peristaltic pump (Ismatec S.A., Spain). The mixture of VOCs was supplied by means of a microburette (Multiburette 2S, Crison Inst. S.A., Spain). The resulting gas stream was split in four and fed to each biofilter from the bottom. Every 12 h 100 mL of tap water was sprinkled over the biofilter beds by means of a Primus 208-18 dosing pump (Alldos GmbH, Germany) and a series of electrovalves, in order to provide additional moisture and to wash dead cells and metabolic side-products of ammonia and VOCs degradation. The control of the pump and the electrovalves was carried out by means of a PC, using a home-made Visual Basic™ application.

2.2. Analytical methods

Gas samples were periodically extracted from the inlet and outlet ports of the biofilters for VOCs and NH_3 analyses. For VOCs determination, two gas chromatographs were employed throughout the study. A calibrated GC 6890N (Agilent Tech. S.A., Spain) equipped with a HP-5 capillary column and a flame ionisation detector (FID) was used for DMS quantification. Calibrations were performed according to Prado et al. [14]. Injector, oven and detector temperatures were 135, 40 (isothermal) and 260 °C, respectively. A split ratio of 5:1 was applied. Analyses of the remaining VOCs (DMDS, α-pinene, hexanal and MIBK) were carried out to determine the removal efficiencies (RE) using a Trace GC-Ultra GC-MS (Thermo Fisher Sci. Inc., USA) equipped with a DB-624 capillary column was used. Samples were stored in 10 cm long × 3.6 cm diameter stainless steel adsorption cartridges packed with Carbotrap C and Carbosieve SIII as adsorbents. Desorption from the cartridges was performed at 45 °C. The temperature was increased at a rate of 5 °C/min, up to 240 °C. The inlet concentration of these four VOCs was calculated based on that of DMS. Due to analytical problems, the concentrations of butyric acid could not be determined. The ammonia concentration was determined by means of a continuous flow analyser [15], after bubbling the gas stream in acidified water in order to absorb all ammonia. A Hygrotest 600 PHT sensor (Inst. Testo S.A., Spain) was used to determine the gas temperature and moisture content. The pressure drop along the beds was measured by means of a glass U-tube manometer.

Leachate samples were periodically collected for analysis from the bottom of each reactor. Conductivity was determined by means of a MicroCM 2100 sensor (Crison Instr. S.A., Spain). A MicropH 2001 sensor was employed for measuring pH (Crison Instr. S.A., Spain). Chloride, N-nitrite, N-nitrate, S-sulphate and P-phosphate concentrations were all determined by means of an ICS-1000 Ion Chromatograph (Dionex Corp., USA), equipped with an IonPac AS9-HC. Absorbance of liquid samples was determined at a wavelength of 550 nm by means of a PU 9620 UV/VIS/NIR spectrophotometer (Philips, The Netherlands).

2.3. Inocula and packing media preparation

An adapted microbial culture was employed as inoculum in BF1, BF2 and BF4, while sludge from a municipal wastewater treatment plant (MWWTP) was used as inoculum for BF3. In order to obtain six specific microbial cultures, 5 g from the packing material (a mixture of compost and a clay-based inert material used as bulking agent) of an odour-treatment industrial biofilter was mixed with 50 mL of different culture media supplemented with moderate concentrations of the aforementioned pollutants. At the industrial biofilter, an average ammonia inlet concentration of around 45 mg/m^3 was treated. Apart from α-pinene, which reached concentrations up to 1850 μg/m^3, the rest of the VOCs never reached values above 250 μg/m^3. Nitrifying bacteria were cultured in a specific nitrification medium [16] and enriched with NH_4Cl. Sulphur-oxidising bacteria were cultured in a solution containing $MgSO_4 \cdot 7H_2O$ (0.16 g/L) and NH_4Cl (0.08 g/L) and enriched with DMS and DMDS. Heterotrophic microorganisms were cultured in a solution containing NH_4Cl (100 g/L), $CaCl_2 \cdot 2H_2O$ (4 g/L), $MgSO_4 \cdot 7H_2O$ (20 g/L) and NaCl (10 g/L) and enriched with α-pinene, hexanal, butyric acid or MIBK. 5 mL/L of a trace element solution [16] was added to each flask weekly. These cultures were incubated at 30 °C under vigor-

Table 1
Gas-phase N-NH_3 concentration and load supplied to each biofilter during the experimental period.

Stage	Days	[N-NH_3] (ppmv)	N-NH_3 load (g/m^3 h)
I	0–14	72 ± 11	6.0 ± 0.1
II	14–33	25 ± 8	2.1 ± 0.7
III	33–44	3 ± 3	0.3 ± 0.3
IV	44–78	98 ± 19	8.2 ± 1.6

ous shaking, and periodically supplied with their corresponding pollutant. In order to avoid overgrowth and metabolic by-product accumulation, an aliquot of 45 mL was substituted from each culture with fresh medium weekly. This process was performed for approximately three months. The resulting adapted culture used as an inoculum was prepared by mixing equal volumes of the six cultures.

The media employed in BF1, BF2 and BF3 were developed by mixing a volume *V* of spherical clay pellets and a volume *V* of compost with *V*/10 of its corresponding inoculum (adapted microbial culture for BF1 and BF2 and MWWTP sludge for BF3) and *V*/10 of $CaCO_3$. The mixture was stirred for 48 h in a cement mixer. Similarly, for BF4, a volume *V* of pine bark was mixed with *V*/10 of the adapted microbial culture and *V*/10 of $CaCO_3$. Calcium carbonate was added in order to buffer the filter media during the first stages of bioreactor operation.

2.4. Microbial characterisation

In order to characterise the original inoculum, the abundance of fungi/yeasts and heterotrophic, sulphur-oxidising and nitrifying bacteria in the industrial biofilter from which the adapted inoculum was produced were determined in a series of plate counts. Samples were extracted at two different bioreactor heights. The bioreactor had a depth of 1 m. Sampling point A was located at a depth of 30 cm, while sampling point B was located at a depth of 70 cm. The extraction of the biomass was performed by mixing 10 g of packing material from the biofilter with 250 mL of de-ionised water. Subsequently, the mixture was shaken over a period of 24 h at a rate of 200 rpm.

A series of Petri plates were prepared and inoculated with the biofilter extract, diluted in a proportion between 10^{-2} and 10^{-6} as in the plate count methodology reported by Madigan et al. [17]. Each set of Petri plates contained a different culture medium: nitrifying bacteria plates contained a specific nitrification medium [16], sulphur-oxidising bacteria plates contained a specific medium (*Thiobacillus thiooxidans* medium, as described in Gerhardt and co-workers [16]), heterotrophic microorganism plates contained BF2A Agar (18.2 g/L) and nystatin dihydrate (50 μg/mL) and fungi/yeasts plates contained potato carrot agar supplemented with Streptomycin sulphate (500 mg/L) and tetracycline hydrochloride (50 mg/L). All the plates were incubated at 30 °C. The number of colonies was counted after reaching 30–300 colonies/plate for bacteria and 3–30 colonies/plate for fungi/yeasts [17]. Incubation time was 36, 60 and 144 h for heterotrophic bacteria, fungi/yeasts and autotrophic bacteria, respectively.

2.5. Operating conditions of bioreactors

The experimental period was divided into four stages, which differed only in the inlet ammonia concentration fed to the biofilters (Table 1). A total VOCs concentration of 20.9 ± 9.1 ppmv was supplied to each reactor at the same time. The VOCs gas mixture contained 18.8% dimethyl sulphide (DMS), 18.8% dimethyl disulphide (DMDS), 18.8% methyl isobutyl ketone (MIBK), 14.5% hexanal, 14.5% α-pinene and 14.5% butyric acid. During the experimental period, a constant gas flow rate of 425 L/h was fed to each biofilter, corresponding to an EBRT of 25 s. The air relative humidity was always above 80%. Biofilters were operated in an upflow mode, at room temperature, and 100 mL of tap water was sprinkled over them every 12 h.

2.6. Nitrification rates and nitrogen balance

Nitritation (R1) and nitratation (R2) rates were calculated as described by Baquerizo et al. [18], while nitrogen recovery (outlet/inlet nitrogen mass ratio, NR) was calculated according to Eq. (1), where $m(\text{N-X})_{out}$ is the sum of the masses of nitrogen as ammonia (both in liquid and in gas phase), ammonium, nitrite and nitrate leaving the bioreactor over a certain period of time (commonly between 48 and 72 h), and $m(\text{N-NH}_3)_{in}$ is the mass of nitrogen entering the system during that same period.

$$\text{NR} = \frac{m(\text{N-X})_{out} \cdot 100}{m(\text{N-NH}_3)_{in}} \quad (1)$$

3. Results

3.1. Inoculum characterisation

Compost extracted from an odour-treating industrial biofilter was employed as the source of microorganisms for the preparation of the adapted inoculum. In order to confirm that the compost contained a sufficient amount of active microbial community, a series of samples extracted at depths of 30 and 70 cm were microbiologically characterised. The results of the cell counts are presented in Table 2.

As expected, heterotrophic bacteria were the most abundant, with values of up to $(7.9 \pm 2.7)\cdot10^8$ CFU/g packing material. On the contrary, fungi/yeast concentration only reached values of around 10^6 CFU/g packing material. Microbial concentrations for sampling point B approximately doubled those of point A for all microbial groups, showing that biomass concentration stratifies from the bottom to the top of the reactor according to the direction of the gas flow, since a higher pollutant concentration is available [1].

During the inoculum preparation in liquid media, an observed specific growth rate (μ_{obs}) was defined as a kinetic parameter to describe the growth of each specific culture during the enrichment period. μ_{obs} was determined by means of Eq. (2), where Abs is the culture absorbance, Abs_0 is the initial absorbance in each weekly cycle and Δt is the interval time per cycle. As previously mentioned, all cultures were diluted in a fresh medium each week in order to eliminate undesirable secondary by-products. During these cycles, 3–5 absorbance measurements were performed. Fig. 2 shows the

Table 2
Microbial abundance at different depths of an industrial biofilter (average value ± standard deviation).

Microbial group	Microbial concentration (CFU/g packing material)		Incubation time (h)
	Sampling point A (30 cm depth)	Sampling point B (70 cm depth)	
Heterotrophic bacteria	$(4.0 \pm 1.6)\cdot10^8$	$(7.9 \pm 2.7)\cdot10^8$	36
Nitrifying bacteria	$(1.0 \pm 0.1)\cdot10^7$	$(2.3 \pm 0.2)\cdot10^7$	144
Fungi/yeast	$(1.7 \pm 0.3)\cdot10^6$	$(3.8 \pm 1.4)\cdot10^6$	60
Sulphur-oxidising bacteria	$(5.9 \pm 0.5)\cdot10^7$	$(9.7 \pm 2.8)\cdot10^7$	144

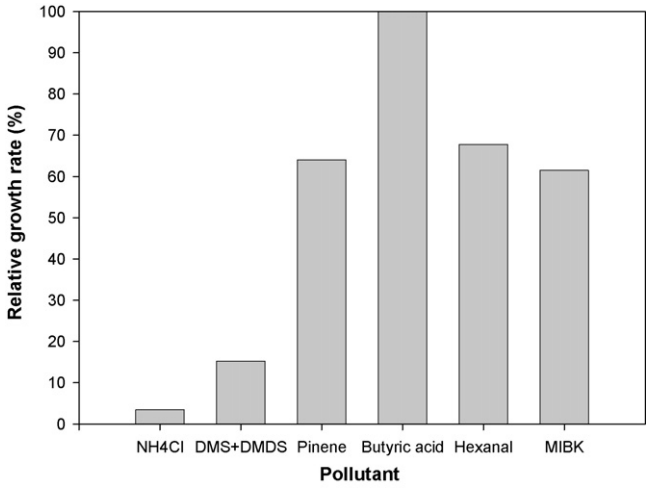

Fig. 2. Estimated relative growth rates for each culture. Data is presented as a percentage referred to the maximal growth rate measured (butyric acid).

relative growth rates for each culture.

$$\mu_{obs} = \frac{\mathrm{Ln}(\mathrm{Abs}/\mathrm{Abs}_0)}{\Delta t} \quad (2)$$

As expected, the flask enriched with NH_4Cl, which is basically degraded by autotrophic nitrifying bacteria, showed the lowest μ_{obs} value (0.07 ± 0.02 1/day), while in the heterotrophic cultures average μ_{obs} values between 1.2 and 2.0 1/day were found. The culture enriched with DMS and DMDS showed a μ_{obs} value of 0.31 ± 0.09 1/day. It is likely that a mixed autotrophic and heterotrophic community might have grown.

3.2. Ammonia treatment

Immediately after the biofilters were packed with the inoculated filter bed material, the supply of pollutant-laden air was started. Analyses of gas-phase NH_3 concentration at the inlet and outlet of the reactors were performed three times a week, starting on day 0. An overview of the ammonia elimination during the whole experimental period for BF1 is presented in Fig. 3.

As Fig. 3a shows, during the first two weeks of operation (stage I), the gas stream fed to BF1 contained an N-NH_3 concentration of around 75 ppmv. An increasing trend in the RE, from 35% (day 0) to around 100% (day 14), was observed during this stage. However, Fig. 3b shows that no clear nitrifying activity could be found during this time. The inlet N-NH_3 concentration was decreased on day 14 of operation and kept at a value of around 25 ppmv for 19 days (stage II). As Fig. 3a shows, the ammonia RE remained close to 100% during this stage. Additionally, immediately after the ammonia load was decreased, the first evidence of nitrifying activity was observed (Fig. 3b). At the end of this stage, N-NO_3^- concentrations above 400 mg/L could be found in the leachate and around 75% of the nitrogen recovered in the drain during this stage appeared as N-NO_3^-. At the beginning of stage III, the inlet N-NH_3 concentration was decreased to around 3 ppmv, with the purpose of washing out the aqueous nitrogen species prior to a sudden increase in the ammonia feed. During this stage, remarkable N-NO_3^- concentrations could still be found in the drain as a result of the carry-over of the nitrate absorbed in the liquid phase inside the reactor or adsorbed in the filter bed. This proves the existence of a delay between alterations in the inlet nitrogen concentration and variations in the nitrogen content in the leachate linked to the nature of the reactor and to the watering frequency of the biofilter. In stage IV, the N-NH_3 concentration was increased to around 100 ppmv. Immediately, nitrification was resumed. A linear increase in the N-NO_3^- concentration in the drain was observed, reaching values of around 900 mg/L at the end of the experimental period (day 78). Also, during the first 12 days after the beginning of this stage, an increase in the production of N-NO_2^-, up to values of around 900 mg/L, was found. By day 78 of operation around 60% of the nitrogen recovered in the drain appeared in an oxidised form (N-NO_2^- or N-NO_3^-).

As expected, results obtained in BF2 were very similar to those found in BF1 (Table 3). The ammonia RE of BF3 was higher than that of BF1 and BF2 during stages I and IV, with average values above 80% throughout the entire study. It was observed that this biofilter presented an important accumulation of stagnant water, which could explain the higher ammonia elimination capacity (EC). This accumulation was probably due to the growth of non-nitrifying microbial strains present in the inoculum. Also, nitratation was strongly inhibited during most of the study in BF3. During this IV stage the N-NO_3^- content rarely exceeded 400 mg/L, less than half of that obtained for BF1 and BF2. Finally, although the N-NH_3 RE of BF4 was very similar to those of BF1–2, no clear evidence of nitrification could be found during the first month of operation. From day 55 onwards, N-NO_3^- concentration in the drain increased slightly, up to values of around 280 mg/L. As Table 4 shows, the nitrifying activity of this bioreactor was very low compared to those of BF1–BF3. It was observed that the amount of biomass attached to this material was also lower than in the rest of the biofilters.

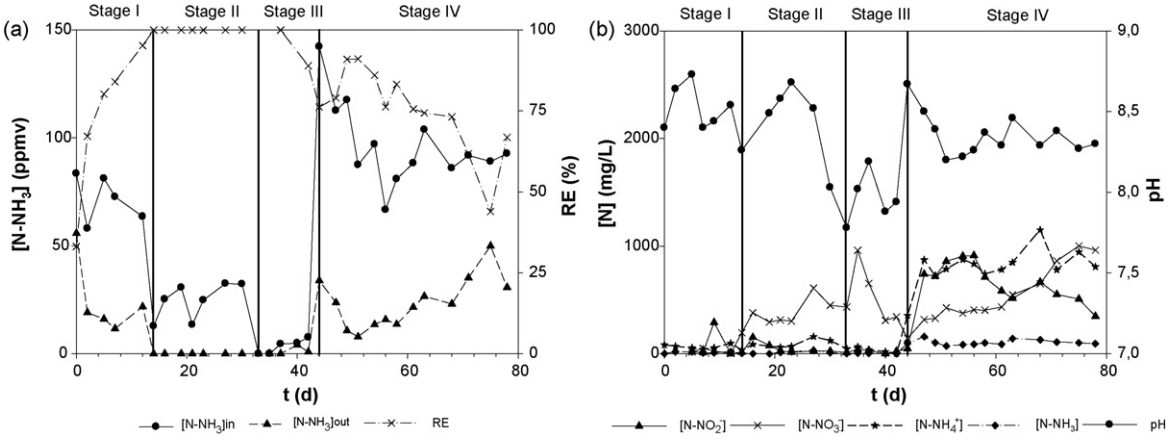

Fig. 3. Evolution of (a) ammonia inlet and outlet concentrations and removal efficiency (RE) in BF1; (b) N-ammonia, N-ammonium, N-nitrite and N-nitrate concentrations and pH in BF1 leachates.

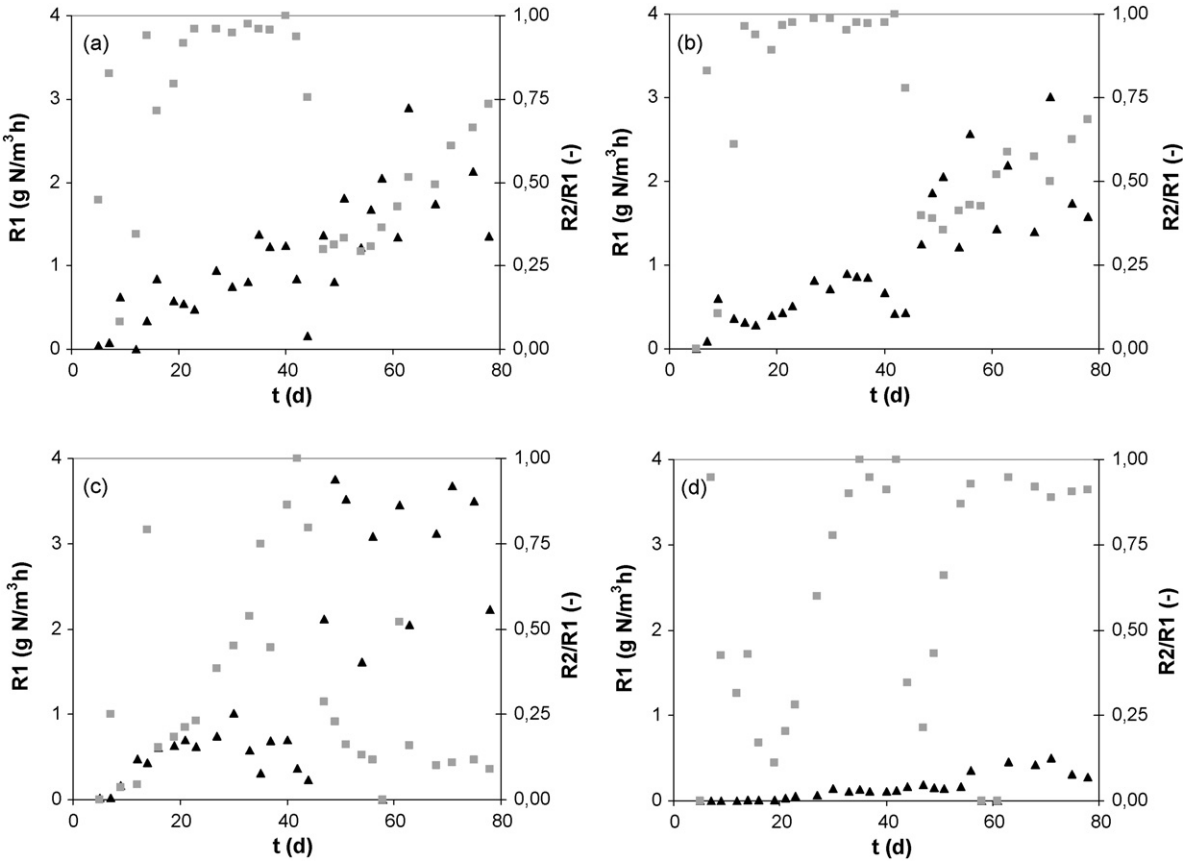

Fig. 4. Nitritation rates (R1, ▲) and nitratation/nitritation ratios (R2/R1, ■) along the experimental period for biofilter BF1 (a), BF2 (b), BF3 (c) and BF4 (d).

Table 3
Bioreactors performance during the experimental period and nitrogen speciation in the leachate in stage IV (average value ± standard deviation).

Stage	Parameter	BF1	BF2	BF3	BF4
I	N-NH_3 EC (g/m^3 h)	3.9 ± 1.3	4.2 ± 1.1	4.7 ± 0.8	5.4 ± 1.4
	N-NH_3 RE (%)	66 ± 23	68 ± 19	80 ± 19	89 ± 13
II	N-NH_3 EC (g/m^3 h)	2.1 ± 0.7	2.1 ± 0.7	2.1 ± 0.7	2.1 ± 0.7
	N-NH_3 RE (%)	100 ± 0	100 ± 0	100 ± 0	100 ± 0
IV	N-NH_3 EC (g/m^3 h)	6.1 ± 1.7	6.1 ± 1.2	8.0 ± 1.7	6.3 ± 2.0
	N-NH_3 RE (%)	74 ± 13	74 ± 9	93 ± 6	74 ± 20
	[N-NH_4^+] (%)	40 ± 6	36 ± 4	40 ± 5	59 ± 9
	[N-NH_3] (%)	5 ± 2	5 ± 4	6 ± 5	15 ± 5
	[N-NO_2^-] (%)	29 ± 1	29 ± 9	43 ± 14	6 ± 5
	[N-NO_3^-] (%)	25 ± 9	30 ± 6	12 ± 8	20 ± 12
	NR (%)	129 ± 39	146 ± 38	56 ± 38	55 ± 33

EC: Elimination capacity. RE: Removal efficiency.

Although all the bioreactors showed a certain nitrifying activity, it must be highlighted that between 40 and 75% of the nitrogen removed from the reactors was merely transferred into the liquid phase instead of biodegraded. Additionally, nitrogen recoveries (NR) were calculated for all four reactors during stage IV. Results (Table 3) show that significant deviations from total recovery (up to 45%) were found in all reactors. The delay between the variations in the inlet ammonia concentration fed to the reactors and the response observed in the leachate could explain the deviation from the ideal 100% NR.

Table 4
VOCs removal efficiency during the experimental period (average value ± standard deviation).

Compound	BF1 RE (%)	BF2 RE (%)	BF3 RE (%)	BF4 RE (%)
DMS	91 ± 6	92 ± 10	89 ± 9	84 ± 9
DMDS	93 ± 8	94 ± 9	89 ± 15	89 ± 12
MIBK	96 ± 4	96 ± 5	95 ± 6	93 ± 8
α-pinene	93 ± 5	93 ± 9	94 ± 8	79 ± 16
Hexanal	96 ± 3	95 ± 5	94 ± 7	92 ± 9
Total	94 ± 4	94 ± 5	91 ± 8	85 ± 6

3.3. Nitrification rates and nitrogen mass balances

Nitritation (R1) and nitratation (R2) rates were calculated for the four reactors throughout the experimental period. In Fig. 4, the nitritation rate and the ratio R2/R1 are plotted against time. R2/R1 represents the ratio between the amounts of nitrate and nitrite produced in the reactor per unit of reactor volume and time. Hence, values close to 1 indicate full nitrification (to nitrate), while values close to 0 represent predominance of partial nitrification (to nitrite). Results obtained for BF1 (Fig. 4a) show that the nitritation rate increased quasi-linearly during the entire experimental period with the exception of stage III, during which the lack of ammonia led to a decrease in this parameter. Maximum R1 values of around 2.5 g N/m^3 h were reached at the end of the experimental period. Also, following a start-up period characterised by relatively low R2/R1 values, this ratio reached values of above 0.9 in the third week of operation, indicating a very high conversion rate of N-NH_4^+ to N-NO_3^-. Such a high R2/R1 ratio was maintained until the beginning of stage IV, during which it decreased to values of around 0.3. This drop in the R2/R1 ratio value was due to the accumulation of N-NO_2^- that was produced as a result of the increase in the N-NH_3 feed started on day 44. However, the reactor's nitrifying activity recovered gradually during stage IV. At the end of the study, R2/R1 ratio values of around 0.75 had been reached. Fig. 4b shows that BF2 and BF1 behaved in a similar way.

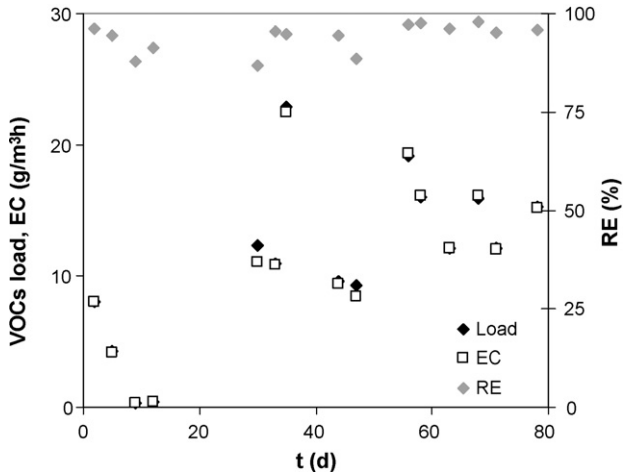

Fig. 5. Total VOCs load fed to each reactor and elimination capacity (EC) and removal efficiency (RE) in BF1.

The results presented in Fig. 4c show the distinctive behaviour of BF3. R1 values close to 4 g N/m^3 h found in this system reflect the more efficient biological oxidation of NH_3 in this system. This is probably due to the higher absorption of ammonia in BF3 due to a higher water accumulation. The R2/R1 ratio in this reactor, which rarely exceeded 0.5, shows that nitratation in BF3 was inhibited. Finally, BF4 showed a very poor nitritation rate during the entire experimental period, never surpassing 0.5 g N/m^3 h.

3.4. VOCs treatment

At the same time as the ammonia supply, a VOCs mixture containing DMS, DMDS, MIBK, butyric acid, hexanal and α-pinene was fed to the bioreactors. Fig. 5 shows the global VOCs load fed to each biofilter and the global VOCs RE and EC for BF1 except for butyric acid (which could not be measured). A significant scattering in the VOC inlet loads was found during stages I–III, with values of between 0.4 and 23 g/m^3 h, due to instability in the VOC feeding system. However, VOC inlet loads were relatively stable during stage IV, with an average value of around 14 g/m^3 h. Regardless of the variable VOC load, the average VOC RE in BF1 and BF2 were higher and more stable throughout the entire study than in BF3 and BF4 (Table 4). Additionally, Table 4 shows that all VOCs were degraded with average efficiencies above 90% except for DMS and α-pinene in BF4, the latter probably due to the emission of this compound from the pine bark. Overall, BF4's performance was slightly worse than that of the other biofilters.

Additionally, the evolution of the pressure drop in all four biofilters was measured during the entire study. The pressure drop in biofilters BF1, BF2 and BF4 remained relatively low during the entire experimental period, never exceeding 22 mm water column/m filter bed. However, in BF3, values of up to 155 mm water column/m filter bed were observed at the end of the study. This was due to the accumulation of water that took place, probably, as a consequence of uncontrolled biomass growth in this biofilter. This was probably due to the inoculation of BF3 with a bacteria-rich inoculum such as MWWTP sludge.

4. Discussion

Although μ_{obs} calculations cannot be compared with literature values, relative growth rates are interesting in terms of assessing the role of the microbial populations in the performance of the biofilter. Cell countings presented in Table 2 and relative growth rates in Fig. 2 show that microorganisms exhibiting chemolithotrophic strategies, such as sulphur-oxidising and nitrifying bacteria, are characterised by presenting lower biomass yields and lower growth rates than heterotrophic bacteria. Furthermore, heterotrophic biomass does not consume the same substrate as autotrophic microorganisms. However, both populations will compete for oxygen, which may lead to nitrifying and sulphur-oxidising activity limitation during biofilter operation.

Fig. 3a and b show an upward trend in the N-NH_3 RE registered during the first two weeks, which was probably due to an increase in the biological activity as well as an increase in the absorption capacity of the biofilter motivated by the periodical irrigations of the filter bed. Biological activity was later proved by the accumulation of N-NO_2^- and N-NO_3^-. Throughout stages II–IV, an increasing nitrifying activity in the biofilter was found. Only two days after the beginning of stage IV, N-NO_3^- concentrations of around 300 mg/L were measured, revealing an adaptation of the nitrifying microbial community to the presence of high concentrations of ammonia. However, as shown in Table 4, the overall relative concentrations of N-NH_4^+ and N-NO_2^- in the drain during stage IV were similar to those of N-NO_3^-, suggesting local inhibitions of ammonium-oxidising biomass (AOB) and nitrite-oxidising biomass (NOB) in the biofilter. Different authors have reported that the activities of both AOB and NOB can be inhibited by the presence of free ammonia (FA, NH_3) or free nitrous acid (FNA, HNO_2) in the liquid phase [18–20]. The inhibition thresholds (concentrations under which 50% of the biomass is inhibited) reported vary greatly, depending mainly on the degree of adaptation of the microorganisms to the inhibiting nitrogen species. Jubany et al. [21] reported inhibition thresholds of 5.8 mg N-FA/L for AOB, 0.16 mg N-FNA/L for AOB, 0.78 mg N-FA/L for NOB and 0.02 mg N-FNA/L for NOB. In the present work, N-FA nitrogen concentrations in the drain of BF1 during stage IV (Fig. 3b) ranged between 75 and 150 mg N-FA/L. Hence, the possibility of inhibition of AOB and NOB in certain regions of the biofilter cannot be neglected. Also, N-FNA nitrogen concentrations remained below 0.04 mg N-FNA mg/L. According to this value, the possibility of NOB inhibition by N-FNA cannot be discarded.

Moreover, biofilter BF3 packed with the same packing material as biofilters BF1 and BF2 but inoculated with MWWTP sludge presented a lower nitrification capacity throughout the experimental period. The nitratation inhibition is likely to be a consequence of NOB inhibition caused by the accumulation of FA and FNA, since N-FA and N-FNA concentrations during stage IV were 140 ± 30 and 0.02 ± 0.01 mg N/L respectively. These results show that the use of a non-adapted inoculum in BF3 led to a poorer nitrite biodegradation activity than when a specifically adapted inoculum was used. Nevertheless, it is important to highlight that the absorption phenomenon was the predominant nitrogen elimination process in all biofilters, which is not unexpected since it has already been observed by different authors [18,22]. However, recent studies have reached ammonia oxidation percentages to nitrate and nitrite of over 50% [7,23]. Furthermore, similar deviations from the ideal 100% of around 30–40% have been found in previous studies [6,24,25,26]. In many cases, these deviations from the ideal can be explained by such biological processes as denitrification, biomass growth or the aforementioned delay. Moreover, nitritation (R1) and nitratation (R2) rates represented in Fig. 4 further demonstrate the higher nitrification capacity of biofilters BF1 and BF2 inoculated with an adapted inoculum compared to biofilters inoculated with MWWTP sludge. The fast adaption of the biomass to the complete biodegradation of N-NH_3 to N-NO_3^- was found in biofilters BF1 and BF2 according to the progressive increase of the ratio R2/R1 during the first 40 days as well as a gradual nitrifying activity recovery of the reactor at the beginning of stage IV.

Results also showed that total VOC RE was maintained at above 85% in all four biofilters during the experimental period regardless of the ammonia fed to the reactor. The inlet ammonia concentration (in the range of 3–100 ppmv), as well as the pH fluctuations, did not affect the VOCs RE. Nevertheless, the biomass growth in the biofilter is mostly due to VOCs biodegradation since the heterotrophic biomass yield is higher than that of nitrifying and sulphur-oxidising biomass. Excessive biomass growth increases the resistance to gas flow and, in turn, may lead to an excessive pressure drop through the biofilter. Even though the filter bed or carrier material price is considered the most significant parameter linked to investment costs in biofiltration [27], the pressure drop is considered to be the major factor that determines the amount of energy needed by blowers to force the contaminated gas through the filter bed material [28,29]. Besides biofilter BF3, the pressure drop values obtained for the other biofilters can be considered low in comparison with values reported for peat, rock wool, fuyolite and ceramic biofilters [30], where values above 25 mm water column/m filter bed were measured. The pressure drop values in BF3 of up to 155 mm water column/m filter bed at the end of the study were a consequence of excessive biomass growth and consequent water accumulation in the bed, which can be related to the complexity of the microbial community of the MWWTP inoculum used. Thus, inoculum again plays a key role not only because it may speed up the start-up of the reactor, but also because operational limitations can be encountered in terms of the excessive development of biomass in the biofilters. No VOC measurements were done in the leachates. Nevertheless, according to Prado et al. (2006), it has been proved that less than 3% of formaldehyde and methanol was transferred to the liquid phase in a biotrickling filter treating loads of formaldehyde and methanol above 100 g/m^3 h [31]. Considering that both methanol and formaldehyde have higher solubility values than the VOCs used in the present work and that VOCs inlet load supplied to the biofilters never overcame 14 $g C/m^3$ h, it is likely that negligible amounts of these VOCs were present in the liquid phase.

5. Conclusions

A new hybrid (organic/inert) packing material was developed and its performance assessed in a series of conventional biofilters for the treatment of complex gas mixtures similar to those emitted in current composting facilities. Considerably higher maximum nitritation rates were reached in the biofilters packed with the new packing material compared to the biofilter packed with pine bark. Also, of the biofilters packed with the new material, those that were inoculated with the adapted microbial culture showed significantly higher nitratation rates and developed a much lower pressure drop than a biofilter inoculated with MWWTP sludge. Overall, results showed that the hybrid packing material is a suitable material for biofiltration if selectively inoculated according to the procedure used in the present work. However, long-term studies need to be undertaken in order to consider other factors such as packing material stability or nutrient depletion. Interestingly, it was observed that only a fraction of between 25 and 60% of the nitrogen found in the leachate of the reactors appeared in an oxidised form (NO_2^- or NO_3^-), proving that sorption can play a significant role in ammonia abatement in conventional biofilters. Accordingly, nitritation rates serve as a better measure of the extent of NH_3 biodegradation in biological reactors than EC.

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