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Title: Comparative assessment of a biofilter, a biotrickling filter and a hollow fiber membrane bioreactor for odour treatment in wastewater treatment plants

Article Type: Research Paper

Keywords: biofilter; biotrickling filter; membrane bioreactor; odour treatment; volatile organic compounds

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Abstract: A low abatement efficiency for the hydrophobic fraction of odorous emissions and a high footprint are often pointed out as the major drawbacks of conventional biotechnologies for odour treatment. In this work, two conventional biotechnologies (a compost-based biofilter, BF, and a biotrickling filter, BTF), and a hollow-fiber membrane bioreactor (HF-MBR) were comparatively evaluated in terms of odour abatement potential and pressure drop (□P) at empty bed residence times (EBRTs) ranging from 4 to 84 s, during the treatment of methyl-mercaptan, toluene, alpha-pinene and hexane at trace level concentrations (0.75 - 4.9 mg m-3). High removal efficiencies (RE > 90% regardless of the air pollutant) were recorded in the BF at EBRTs ≥ 8 s, although the high □P across the packed bed limited its cost-effective operation to EBRTs > 19 s. A complete methyl-mercaptan, toluene and alpha-pinene removal was recorded in the BTF at EBRTs ≥ 4 s and □P lower than 33 mmH2O (~611 Pa mbed-1), whereas slightly lower REs were observed for hexane (~88%). The HF-MBR completely removed methyl-mercaptan and toluene at all EBRTs tested, but exhibited an unstable alpha-pinene removal performance as a result of biomass accumulation and a low hexane abatement efficiency. Thus, a periodical membrane-cleaning procedure was required to ensure a steady abatement performance. Finally, a high bacterial diversity was observed in the three bioreactors in spite of the low carbon source spectrum present in the air emission.

Cover Letter, For Editor only

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Dear Editor,

Please find enclosed the revised version of our manuscript "**Comparative assessment of a biofilter, a biotrickling filter and a hollow fiber membrane bioreactor for odour treatment in wastewater treatment plants**" co-authored by Raquel Lebrero, Ana Celina Gondim, Rebeca Pérez, Pedro Antonio García-Encina and Raúl Muñoz. The paper is re-submitted for publication in **Water Research** after a careful revision according to reviewers´ suggestions and comments.

Packed bed-based biotechnologies for odour treatment such as biofilters (BFs) and biotrickling filters (BTFs) are claimed to support low removal efficiencies for the hydrophobic fraction of malodorous emissions as a result of mass transfer limitations. In this context, the operation of BFs and BTFs under non-mass transfer limiting conditions requires process design at high gas residence times, resulting in prohibitive land requirements. In this context, the quest for new bioreactor configurations that guarantee a cost-effective treatment of the hydrophobic fraction of the odorous emission has become a hot topic in recent years. Hollow fiber membrane bioreactors (HF-MBR) are compact systems which offer high specific surface areas in a reduced reactor volume, improving simultaneously the transport of oxygen and odorants from the gas phase to the biofilm. However, the implementation of HF-MBRs for gas treatment is very scarce, with no study focused on odour removal. This novel study comparatively evaluated a BF, a BTF and a HF-MBR for the treatment of a mixture of odorants at trace level concentrations in terms of abatement performance and energy requirements. Whereas the results obtained in this study ranked the BTF as the most cost-effective biotechnology, the expected mass transfer enhancement in the HF-MBR for the most hydrophobic odorants was not observed. This study also identified the main niches of research in the application of HF-MBRs for odour treatment (i.e. membrane material selection and biomass accumulation and clogging). The experimental findings here obtained were also supported by an abiotic VOC mass transfer characterization of the HF-MBR and molecular biology techniques (DGGE).

We look forward to your evaluation.

Best regards,

Valladolid, 27 September 2013

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Title: Comparative assessment of a biofilter, a biotrickling filter and a hollow fiber membrane bioreactor for odour treatment in wastewater treatment plants.

Co-authored by Raquel Lebrero, Ana Celina Gondim, Rebeca Pérez, Pedro A García-Encina, Raul Munoz.

Dear Editor,

First, I would like to thank you for the attention you gave to our research article. The manuscript has been revised and modified in accordance to most reviewer's suggestions. More specifically:

REVIEWER 1

General comments

1. This is an interesting comparative study on the performance of different biofilter configurations to treat two main odorants, with one reactor having a potentially reduced footprint.

2. The study was informed and justified appropriately regarding several key parameters such as amelioration efficiency (RE). Examples of projected or calculated performances were provided e.g. Line 391 - 391 to support specific experimental findings. These demonstrated the envisaged potential for extrapolation to pilot and industrial scale applications.

3. Bioreactor configurations, operational parameters and performance efficiencies were then explored in relation to the underpinning microbial community structure/composition with the application of DGGE, Shannon-Weiner diversity and evenness indices, and sequencing. These data were used robustly and successfully to explain, present and support plausible reasons/reasoning for the observed performances of the reactors/biofilter configurations.

4. Overall, the paper presented a topical, interesting, sound and robust experimental design and study. The use of cross-disciplinary analytical methods has built on the established biofiltration knowledge. I, therefore, recommend that the paper is accepted for publication with minor corrections as indicated below.

The authors acknowledge the encouraging comments from Reviewer 1 and carefully revised the manuscript according to his recommendations/suggestions.

Recommended Corrections

1. Check citation format: i.e. comma after et al. or not? See line 42, 433, 466 and 471 for some glaring examples.

The authors apologize for the inaccuracy in the citation format. Citation format was revised and corrected throughout the entire text according to the Reference style of Water Research (for example in current page 3, lines 55-56: "…operation experience (Iranpour et al., 2005; Kraakman et al., 2011)".

2. Line 248: Replace "despite" with "although" for more accurate grammar.

The term "despite" was replaced by "although" in the revised version of the manuscript (current page 12, line 267): "Hence, although the BF was able to maintain MeSH, toluene…".

3. Line 259: Should the sentence read "A subsequent ... of the ... REs..." with the REs in plural instead of singular RE?

The plural form for the acronym RE (REs) was included in the revised version of the manuscript (current page 13, line 277): "A subsequent deterioration of the toluene and hexane REs was observed…".

4. Line 261 Shold these data be "... toluene RE of 98.0 ... and hexane RE of 93.7 ...."?

The singular form of the acronym RE was employed in this revised version of the manuscript as suggested by Reviewer 1 (current page 13, line 278): "steady toluene RE of 98.0 ± 0.7% and hexane RE of 93.7 ± 0.7%".

5. Line 266: Missing an 'm' for 1.3 mM ...

No "m" was missing in the original manuscript since the deterioration of the compost was so severe that the pressure drop increased up to 1.3 m of H_2O column.

6. Using "Fig" or "Figure" in the text and legends?

The term "Fig." was standardized in this revised version of the manuscript and used throughout the complete manuscript: page 29, Figure captions.

7. Unless I am mistaken, the figure legends were missing in the submission.

The legends were not included below the figures in the original submission for clarification purposes since they already contained too much data, but they were included in a separate page devised to Figure captions right after the Reference section.

8. Line 455: Perez Pantoja or Perez-Pantoja?

The authors apologize for this mistake and the family name of the author was corrected in the text (current page 21, line 485): "...for aromatic compounds (Pérez-Pantoja et al. 2011)."

9. The Kristiansen et al. (2011) reference is out of alphabetical order (Line 537-539)

The reference was placed in the correct position in this revised version of the manuscript (current page 25, line 565-567) after Kraakman et al. (2011).

REVIEWER 2

I congratulate the authors with the outcomes of their hard work. The paper will be a valuable contribution when the below comments are addressed in a satisfying manner.

The authors acknowledge the positive evaluation from Reviewer 2 and carefully revised the manuscript according to his comments/suggestions.

Necessary to address:

Research Highlight/Conclusions: Membrane clogging limited the abatement of alpha-pinene and hexane. This conclusion is not supported by clear facts. ? How is it proven that alpha-pinene and hexane limited performance is the result of membrane clogging? Please explain better and address this in discussion or change the conclusion.

The limitation of alpha-pinene abatement as a result of membrane clogging was clearly demonstrated by the deterioration of alpha-pinene removal concomitantly with the formation of a thicker biofilm (macroscopically observed by the increase in the pressure drop on the gas side), and the subsequent improvement in the removal efficiency of this terpene after each membrane cleaning. However, the authors agree with Reviewer 2 on the fact that the limited hexane performance recorded cannot be attributed to membrane clogging due to the lack of a clear correlation. An explanatory remark was included in the revised version of the manuscript (current page 19, lines 425-427): "This phenomenon was more evident for alpha-pinene, whose RE significantly decreased due to membrane clogging and increased subsequently to each membrane cleaning." Therefore, the conclusions and the research highlights were modified accordingly: (page 22, line 515-517) "…the low performance of alpha-pinene being associated to membrane clogging due to biomass overgrowth" and Research Highlight 4 "Membrane clogging limited the abatement of alpha-pinene".

Research Highlight/Conclusions: The high microbial diversity ensured an efficient and stable long-term operation? This

conclusion cannot be drawn from this work. Please explain better why in this case it can be concluded, address this in discussion or change the conclusion.

This statement was modified in the revised version of the Research Highlights: "The reactors showed a high microbial diversity in spite of the low C source spectrum". No reference to this issue was included in the original conclusion section.

Page 21 Line 402: It was hypothesized that the accumulation of biomass in the MBR lumen increased the pressure of the recycling liquid, which compressed the thin silicone tubes, decreasing the cross sectional area and subsequently reducing the actual gas residence time and increasing the <DELTA>P of the odorous emission. ? why has this not been tested? This would be very easy to do I would imagine? This can even be tested under abiotic condition and I suggest researching this and adding these results to make the paper more complete.

The authors agree with Reviewer 2 on the relevance of measuring the increase in the pressure of the recycling liquid as a function of biomass growth. Unfortunately, this analysis was not performed during the operation of the bioreactor and the authors are not able to perform it now since the membrane was broken to draw a biomass sample for microbiological analyses. However, the fact that the accumulation of biomass entailed an increase in the pressure of the recycling liquid was supported by visual observations. In this sense, when excessive biomass accumulated, the maximum trans-membrane pressure was exceeded and part of the recycling liquid filtered to the gas side, which decreased the liquid volume in the recirculation tank. At this point, the membrane was cleaned by increasing the liquid recycling velocity. Moreover, the influence of biomass accumulation on the pressure drop of the odorous emission can be clearly observed by the steady decrease in pressure drop after each membrane cleaning (Figure 4C).

Page 22 Line 430: ? question: To overcome clogging of biomass, has increasing the liquid rate been tested (as proposed and proven to be effective by Studer, 2005)). Please include this topic including reference in the discussion. Studer, M.H. (2005) Novel membrane based biological waste gas treatment systems. Dissertation. Swiss federal Institute of Technology Zurich.

A more detailed description on the membrane cleaning procedure was included in the Materials and Methods section of this revised manuscript (current page 7, lines 149-153): "Several membrane cleanings were performed at days 21, 39, 72, and 102 in order to overcome biomass clogging by increasing the liquid recycling rate, which promoted biofilm sloughing due to the increased shear forces. This procedure was successfully implemented in previous studies (Lebrero et al. 2013, Studer 2005)". The reference section was modified accordingly (page 27, lines 609-610): "Studer, M.H., 2005. Novel membrane based biological waste gas treatment systems. Dissertation. Swiss federal Institute of Technology Zurich".

Important to address:

Page 6 line 39: ...emitted from wastewater treatment ? the problem of atmospheric pollution is more general and not limited to wastewater treatment and I suggest stating the problem more general and use wastewater references as an example where the emissions are often different

because of their complex mixtures, low concentrations but large air volumes. So broader the problem of emitting air pollutants and include also other industries.

The authors agree with Reviewer 2 on the broader nature of odour pollution. Additional references to other odour sources apart from wastewater treatment plants were included in the Introduction section (current page 3, lines 39-44): "Malodours emitted from a wide variety of sources (wastewater treatment, landfilling and composting , meat rendering, petrochemical refining, food processing, pulp and paper manufacturing, etc.) are not only a direct threat for human health and wellbeing, but also contribute to photochemical smog formation and particulate secondary contaminant emission (Capelli et al., 2008; Shareefdeen et al., 2002; Sucker et al., 2008)". The reference section was modified accordingly: (page 24, lines 535-537) "Capelli, L., Sironi, S., Del Rosso, R., Céntola, P., Grande, M., 2008. A comparative and critical evaluation of odour assessment methods on a landfill site. Atmospheric Environment 42, 7050-7058" and (page 27, line 613-615) "Shareefdeen, Z., Herner, B., Wilson, S., 2002. Biofiltration of nuisance sulfur gaseous odors from a meat rendering plant. Journal of Chemical Technology and Biotechnology 77, 1296-1299".

The specific reference to malodorous emissions from wastewater treatment plants was also removed from the original manuscript (former pages 4, lines 65-66): "cost-effective treatment of the hydrophobic fraction of the odorous emissions *in wastewater treatment plants*"

Page 6 line 43: low concentrations? add that emissions from wastewater treatment are usually relatively large volumes of air and facilities that can be found in every city.

A brief remark regarding the large volumes of malodorous air emitted from a wide range of facilities in a number of different places was included in this revised version of the manuscript as suggested by Reviewer 2 (current page 3, lines 46-49): "These malodorous emissions are complex mixtures of odorants including sulfur derived and volatile organic compounds (VOCs) at low concentrations (µg m^{-3}-mg m^{-3}) compared to those emitted from industrial processes, and comprise large volumes of air released from widespread common facilities. These characteristics differentiate malodorous from industrial emissions and hinder their cost-efficient abatement".

Page 7 line: 62: suggestion to add: without increase the energy and/or cost to overcome the mass transfer limitation.

This explanatory remark was included in the text as recommended by Reviewer 2 (current page 4, lines 65-66): "…cost-effective treatment of the hydrophobic fraction of the odorous emissions without increasing the energy and/or cost to overcome the mass transfer limitation."

Page 7 line 64: circulating through ? replace by transferred on

The polluted air actually circulates through one side of the membrane, from where pollutants are transferred. This explanatory remark was included in this revised introduction to avoid further misunderstandings (current page 4, lines 67-70): "Advanced membrane bioreactors (AMBR) are based on a membrane-mediated separation between the polluted air emission circulating through

one side (from where pollutants are transferred) and the microbial community attached on the other side of the membrane…"

Page 7 Line 69: increases the local concentration gradients ? of what (pollutants ?) and explain how.

The presence of a biofilm or a culture in suspension on the liquid side of the membrane able to degrade the target pollutant will increase the pollutant concentration gradient by its continuous removal (therefore its concentration in the biofilm will tend to zero). An explanatory remark was included in this revised version of the manuscript for clarification purposes (current page 4, line 74): "…increases the local concentration gradients of the pollutants degraded by the microorganisms".

Page 7 Line 79: in terms of abatement efficiency and pressure drop ? replace by in terms of abatement efficiency and energy consumption (pressure drop)

The corresponding sentence was modified in this revised version of the manuscript as suggested by Reviewer 2 (current pages 4-5, lines 84-85): "…treatment in terms of abatement efficiency and energy consumption (pressure drop)…"

Page 8 Line 98: commercial hollow-fiber module ? describe here what the characteristics are in terms of membrane material (PDMS?), membrane thickness and internal fiber diameter and number of fibers per module.

The specifications of the membrane module used were included in the Materials and Methods section as requested by Reviewer 2 (current page 5, lines 103-105): "The HF-MBR was a commercial hollow-fiber module (PermSelect® PDMSXA-8300 cm^2 module, MedArray Inc., USA) with a total volume of 300 mL. The membrane was made of PDMS (silicone) and consisted of 10600 fibers (internal diameter = 190 µm, wall thickness = 55 µm) with a total membrane area of 8300 cm^2".

Page 9 Line 111: trickling solution? replace by recycling solution (assuming that the solutions of both BTF and AMBR are pH adjusted) trickling solution here gives the impression that only the recycling solution of the BTF was pH adjusted.

The authors modified the former sentence in order to avoid any further misunderstanding and replaced "trickling solution" by "recycling solution" as suggested by Reviewer 2 (current page 6, line 118): "The pH of both recycling solutions was manually controlled at ~7 by daily addition of a 10 g L^{-1} NaOH solution".

Page 10 Line Kaldness K1 ? specify characteristics like material, diameter, surface area.

The characteristics of the Kaldness K1 plastic rings were included in the Materials section of this revised version of the manuscript (page 7, lines 144-145): "Kaldnes K1 plastic rings (polyethylene, diameter = 0.9 cm, surface area = 500 m^2 m^{-3}, Evolution Aqua Ltd., UK)."

Page 11 Line 141: similar EBRT ? explain how the EBRT of the AMBR is defined here (e.g. using the volume of the membrane module or the volume of the sum of all fibers. Explain what power compression means?

The EBRT in the membrane bioreactor was calculated using the total volume of the membrane module. An explanatory remark was included in this revised version of the manuscript for clarification purposes: (page 7, line 149) "HF-MBR was evaluated at similar EBRTs (43, 34 and 16 s, calculated using the total volume of the membrane module) for 95 days". A more detailed explanation on the calculation of the compression energy requirements is now included in the Materials & Methods section of the manuscript (page 9, lines 182-187): "The compression energy requirements at each EBRT were calculated using the following expression to obtain the power requirements (P, W):

$$P = \frac{F \times \Delta P}{0.7}$$

Where F corresponds to the volumetric gas flow rate at each EBRT (m^3 s^{-1}) and ΔP to the pressure drop measured across the packing media at the corresponding EBRT (Pa m_{bed}^{-1}). A standard blower efficiency of 0.7 was considered (Estrada et al., 2012)".

Page 15 Line 171: higher acclimation times compared to the BF were due to the lack of an inherent microbial diversity as that present in the compost ? how do you know, where is did proven? I suggest to change into higher acclimation times compared to the BF were likely due to the lack of an inherent microbial diversity and adsorption to organic matter as that present in the compost (when not measured but only tried to explain than this sentence should also be transferred to the section Discussion)

The higher initial microbial diversity of the BF was supported by the higher Shannon diversity index measured for the mixture activated sludge - compost. Besides, some authors have demonstrated that despite WWTP sludge is often a highly diverse inoculum, the indigenous microbial species present in compost are crucial for the biodegradation of VOCs in biofilters (Prenafeta- Boldu, F.X., Guivernau, M., Gallastegui, G., Viñas, M., de Hoog, G.S., Elías, A., 2012. Fungal/bacterial interactions during the biodegradation of TEX hydrocarbons [toluene, ethylbenzene and p-xylene] in gas biofilters operated under xerophilic conditions. FEMS Microbiology Ecology 80(3), 722.734). An explanatory remark was however included in this revised version of the manuscript as suggested by Reviewer 2 (current page 13, lines 288-291): "This significantly higher acclimation times compared to the BF were likely due to the lack of an inherent microbial diversity (as shown by the lower Shannon diversity index of the activated sludge without compost) and adsorption to organic matter as those present in the compost".

Page 17 Line 316:

Liquid samples from the BF were only withdrawn during the first 30 days of experimentation due to the lack of leachate from that day on. ? (improve English) by e.g. Liquid samples from the BF were only taken during the first 30 days of the experiment due to the absence of leachate from that day on.

The sentence was modified in the revised version of the manuscript as suggested by Reviewer 2 (current page 15, lines 337-338): "Liquid samples from the BF were only taken during the first 30 days of experimentation due to the absence of leachate from that day on."

Page 18 Line 331: What was the pH of all reactors during the experiment? This is important information which should be included. The pH of the liquid phase as well as the biofilm layer should have been measured and reported. pH of the biofilm layer in especially the AMBR would be very useful to possibly explain the inconsistent results in performance. The inconsistent performance of the AMBR have been poorly discussed and is a missed opportunity to increase the quality of this paper.

The authors apologize for this oversight and included in the Results section of this revised manuscript the results from pH analysis for the three bioreactors: the BF (page 15, lines 338-339): "During that period, a decrease in the pH from 4.7 to 4.2 was recorded", the BTF (page 15, lines 346-347): "The pH remained stable at 6.85 ± 0.17 in this recycling medium during the complete experimentation period, while sulphate concentration increased …" and the HF-MBR (page 16, lines 350-351): "The pH in the MBR recycling medium was maintained at 6.92 ± 0.20 and the sulphate concentration…". The authors agree with Reviewer 2 on the relevance of measuring the local pH of the biofilm layer, which could provide key information on the performance of the bioreactors. However, this measurement was not possible due to the difficult access to biofilms in the reactors. For instance, the periodical sampling of biomass aliquots inside the packed reactors would have entailed bed unpacking and subsequent packing mixing, likely altering the performance of the bioreactors. Similarly, it was not possible to sample the biofilm formed over the thin fibers of the MBR. Nevertheless, the continuous liquid recycling at a neutral pH, the periodic membrane cleanings and the reduced thickness of the biofilm probably maintained a nearly neutral pH in the biofilm layer. The inconsistent alpha-pinene removal performance of the HF-MBR was attributed to the periodic membrane clogging, which was supported by the experimental results (increase in alpha-pinene removal after membrane cleaning and a progressive decrease concomitant to biomass accumulation). This was further clarified in this revised version of the manuscript (current page 19, lines 422-427): "In addition, the formation of a thick biofilm on the membrane created an additional mass transfer resistance, which likely resulted in a deterioration of the membrane performance. This phenomenon was more evident for alpha-pinene, whose RE significantly decreased due to membrane clogging and increased subsequently to each membrane cleaning."

Page 18 Line 338: How can the slightly lower diversity index of 2.8 (Fig. 7) in biofilter at the end of the experiment be explained. pH, salt accumulation or else ?

The low bacterial diversity index recorded for the biofilter at the end of the experiment was attributed to an increase in the fungal population as hypothesized in the manuscript (former page 19, lines 437-441): "This decrease in diversity could be attributed to the proliferation of fungi and the subsequent increase in the fungal/bacteria ratio, whilst the presence of fungi was not analyzed in this study. The increase in the fungal biomass during the operation of organic-packed BFs has been previously reported by Prenafeta-Boldú et al. (2012) in a BF treating toluene". A decrease in the pH or the accumulation of salts in the packing material could have also contributed to this hypothetic increase in the fungal/bacterial ratio. A brief explanation was included in this revised manuscript as suggested by Reviewer 2 (current page 20, lines 465-468): "This decrease in diversity could be attributed to the proliferation of fungi and the subsequent increase in the fungal/bacteria ratio likely mediated by pH decrease or excessive salt accumulation in the packing material, but the presence of fungi was not analyzed in this study."

Page 19 Line 433: Reference Friedich correct (Friedich or Friedrich?).

The family name of the first author in reference cited was corrected in the revised version of the manuscript (current page 20, line 461): "…treating low odorant concentrations (Friedrich et al., 2002; Lebrero et al., 2011).".

Page 20 Line 388: Moreover, even at the low EBRTs applied in BTFs, the high flow rates of odorous emissions to be treated still result in large bioreactor volumes: for instance, the treatment of 50000-100000 m3 h-1 would require a BTF volume of 50-110 m3 at an EBRT of 4 s. ? unsure why this sentence is here (to justify research of AMBR application?). 50 -100 m3 reactor volume is not large and usually not a limitation especially as media high can be several meters high resulting in only app. 10-30m2 of reactor footprint. I suggest to remove this sentence or otherwise clarify improve the point you want to make.

This sentence was included in the original manuscript to highlight one of the main drawbacks of biological technologies for odour treatment: their high footprint required even at the low EBRTs applied in BTFs. This could limit the implementation of bioreactors in facilities with space limitations, thus development of compact technologies is of key importance as highlighted in the Introduction section (former page 3, lines 57-60). The sentence was however removed to avoid any further misunderstanding as suggested by Reviewer 2 and a brief explanation was included instead in the revised version of the manuscript (current page 18, lines 406-408): "Moreover, even at the low EBRTs applied in BTFs, the high flow rates of odorous emissions to be treated still result in large bioreactor footprints, hindering their implementation in facilities with space limitations".

Page 21 Line 402: It was hypothesized that the accumulation of biomass in the MBR lumen increased the pressure of the recycling liquid, which compressed the thin silicone tubes, decreasing the cross sectional area and subsequently reducing the actual gas residence time and increasing the <DELTA>P of the odorous emission. ? why has this not been tested and proved to be correct. This would be very easy to do I would imagine? This can even be tested under abiotic condition I suggest to research this and add these results to make the paper more complete.

The authors agree with Reviewer 2 on the relevance of measuring the increase in the pressure of the recycling liquid as a function of biomass growth. Unfortunately, this analysis was not performed during the operation of the bioreactor and the authors are not able to perform it now since the membrane was broken to draw a biomass sample for microbiological analyses. However, the fact that the accumulation of biomass entailed an increase in the pressure of the recycling liquid was supported by visual observations. In this sense, when excessive biomass accumulated, the maximum trans-membrane pressure was exceeded and part of the recycling liquid filtered to the gas side, which decreased the liquid volume in the recirculation tank. At this point, the membrane was cleaned by increasing the liquid recycling velocity. Moreover, the influence of biomass accumulation on the pressure drop of the odorous emission can be clearly observed by the steady decrease in pressure drop after each membrane cleaning (Figure 4C).

Page 21 Line 415: In addition, the formation of a thick biofilm on the membrane created an additional mass transfer resistance, which likely resulted in a deterioration of the membrane performance. ? I can't agree with this explanation. The most active biomass is located at the membrane site (and not the liquid site) of the liquid recirculation stream correct? Mass transfer through a thicker biomass is therefore not necessary unless specific micro-organisms targeting specific VOCs (e.g. alpha-pinene) is limited by a faster growing microbial community consuming other VOCs at higher loading rates? Please reply and include in the discussion.

As already mentioned, the accumulation of biomass on the membrane resulted in a deterioration of the alpha-pinene removal performance. This phenomenon was highlighted in this revised version of the manuscript to avoid further misunderstandings (current page 19, lines 423-427): "In addition, the formation of a thick biofilm on the membrane created an additional mass transfer resistance, which likely resulted in a deterioration of the membrane performance. This phenomenon was more evident for alpha-pinene, whose RE significantly decreased due to membrane clogging and increased subsequently to each membrane cleaning". The limitation in mass transfer performance was related to an increase in the liquid pressure drop, which resulted in water diffusion towards the gas side.

Page 22 Line 430: Questions: To overcome clogging of biomass, has increasing the liquid rate been tested (as e.g. suggested and proven to be effective by Struder, 2005). Please include in the discussion.

A more detailed description on the membrane cleaning procedure was included in the Materials and Methods section of this revised manuscript (current page 7, lines 149-153): "Several membrane cleanings were performed at days 21, 39, 72, and 102 in order to overcome biomass clogging by increasing the liquid recycling rate, which promoted biofilm sloughing due to the increased shear forces. This procedure was successfully implemented in previous studies (Lebrero et al. 2013, Studer 2005)". The reference section was modified accordingly (page 27, lines 609-610): "Studer, M.H., 2005. Novel membrane based biological waste gas treatment systems. Dissertation. Swiss federal Institute of Technology Zurich".

Page 30 Line 604: explain Figure 4D better (and use the same symbols for the different systems as in Figure 4 A, B and C).

Figure 4D was modified in accordance to Reviewer 2 suggestions using similar symbols for the biofilter, the biotrickling filter and the membrane bioreactor as those employed in figures 4A, B and C. The figure caption was also modified and a clearer explanation was included (current page 29, lines 639-646): "**Fig. 4.** Time course of the pressure drop in the biofilter (♦, A), the biotrickling filter (□, B) and the membrane bioreactor (○, C). Dashed vertical lines represent the changes in EBRT, the continuous vertical line in figure 4A the change in the biofilter irrigation rate and the vertical dotted arrows in figure 4C the membrane cleanings. Figure 4D represents the compression energy requirements in the biofilter (♦, dashed line), the compression and pumping energy requirements in the biotrickling filter (□, dotted line) and the membrane bioreactor (○, no line), and the maximum compression energy requirements (continuous line) at different EBRTs".

Page 38 Figure 4D: The power consumption in Watt doesn't say that much about viability. I suggest expressing energy consumption in energy consumption per treatment amount of air (W/m3 h-1) or per treated amount of VOCs (W/g h-1).

Power consumption was calculated based on the maximum pressure drop recorded for each bioreactor at each EBRT, by multiplying this ΔP by the corresponding flow rate in order to estimate the total energy consumption (considering a blower efficiency of 0.7). The authors agree with Reviewer 2 on the fact that expressing the energy consumption per treated amount of VOCs would be interesting, however this calculation was not feasible since the HF-MBR presented a rather unstable performance and a steady value for the amount of VOC treated could not be obtained. However, an explanation on the calculations performed was included in the Materials and Methods section for clarification purposes (current page 9, lines 182-187): "The compression energy requirements at each EBRT were calculated using the following expression to obtain the power requirements (P, W):

$$P = \frac{F \times \Delta P}{0.7}$$

Where F corresponds to the volumetric gas flow rate at each EBRT (m^3 s^{-1}) and ΔP to the pressure drop measured across the packing media at the corresponding EBRT (Pa m_{bed}^{-1}). A standard blower efficiency of 0.7 was considered (Estrada et al., 2012).

REVIEWER 3

The manuscript compares the performances of a biofilter, a biotrickling filter and a hollow fiber membrane bioreactor to eliminate a mixture of four compounds of diverse chemical and physical properties associated with odors from wastewater treatment plants. The paper is well written and presents positive results and I consider that the work merits publication but also recommend that the following issues be properly addressed:

- In general, the results section is overly descriptive, authors should try not to 'repeat' the otherwise clear graphs, but highlight only the relevant information.

The Results section was carefully revised in accordance to Reviewer 3 recommendation and the numerical data provided was significantly reduced to avoid the repetition of redundant information (for example page 12, lines 267-268: "BF was able to maintain MeSH, toluene and alpha-pinene REs > 98% and…"; page 12, line 271: "…initial deterioration in the removal capacity of the biofilter by day 57…"; page 13, lines 276-277: "A subsequent deterioration of the toluene and hexane REs was observed followed by…"; pages 13-14, lines 298-298: "…and steady REs > 97% for MeSH, toluene and alpha-pinene were immediately achieved…", etc.). The Results section was reduced by approximately 10%.

-Which are the values of void and membrane volumes and the exchange surface of the fibers per unit volume (m2/m3). Please include them in section 3.1.

A more detailed description of the membrane module, including the volume and the membrane surface area, was included in this revised section of the manuscript as requested by Reviewer 3 (current page 5, lines 103-105): "The membrane was made of PDMS (silicone), and consisted of 10600 fibers (internal diameter = 190 µm, wall thickness = 55 µm) with a total membrane area of 8300 cm^2".

- Considering the above, how equivalent are the EBRTs as a measure to compare results among the 3 systems? It is clear that the actual residence time is determined by the gas flow and the void volume, which varies amply in the 3 systems. Furthermore, the transfer step to the liquid biotic phase that is required for degradation may be limited by the surface, specially for the sparely soluble gases. The comparison among the systems may yield different results if, say, it is based not on the EBRT but on the exchange surface. I think the paper needs a better discussion on this point.

The empty bed residence time is commonly used as the main operation parameter for bioreactors treating odorous emissions and it is usually employed for comparison purposes. The authors agree with Reviewer 3 on the fact that the actual gas residence time (taken into account the real volume available for air circulation, i.e. the porosity of the packing materials) in the three bioreactors is clearly different and much lower for the membrane bioreactor. However, similar EBRTs were implemented in an attempt to operate the three bioreactors under similar conditions. Besides, the advantages of the membrane bioreactor rely on a higher surface area for mass transfer per unit volume of reactor, and similar REs were observed for MeSH, toluene and alpha-pinene compared to those obtained in the BF and the BTF in spite of the lower actual gas residence time.

This rationale was included in the revised version of the manuscript (current page 20, lines 450-457): "Thus, although membrane bioreactors constitute a promising alternative for treating gaseous emissions containing soluble and moderately soluble VOCs such as MeSH, toluene or alpha-pinene when clogging problems are overcome, the potential performance enhancement for the removal of hydrophobic compounds was not observed. At this point, it is important to remark that the actual residence time of the membrane bioreactor (calculated as the real volume available for gas circulation divided by the gas flow rate) is much lower compared to those of the BF and the BTF. In this sense, the EBRT must be multiplied by 0.72, 0.96 and 0.14 (void volume of the BF, the BTF and the HF-MBR, respectively) in order to obtain the actual gas residence time in each bioreactor. The low gas residence time in the HF-MBR could have mediated the lower hexane removal performances recorded in this system".

- Include and discuss the liquid pumping costs in the economic evaluation. Here there might be also an increase in dP with time in the MBR.

The liquid pumping costs were calculated for the BTF and the HF-MBR assuming a constant pressure drop in the liquid side of 1 bar, since it was not recorded during the experiment. A pumping energy requirement of 0.39 and 0.55 W was obtained for the BTF and the HF-MBR, respectively, regardless of the EBRT tested. This value was added to the gas pumping requirement in Figure 4, representing the overall power consumption for the operation of both bioreactors. A brief remark on the calculation of the liquid pumping costs was included in this revised version of the manuscript (current page 9, lines 187-189): "The liquid pumping costs

were also calculated for the BTF and the HF-MBR assuming a constant pressure drop for the liquid of 1 bar". Figure 4D was modified accordingly. However, it is important to highlight that liquid pumping costs are negligible in the HF-MBR compared to gas compression (0.55 W vs. 60-180 W), corresponding to less than 1%.

- Include a brief discussion on the Elimination Capacities and compare with literature data.

The Elimination Capacities were not provided in the original manuscript based on the low values of the inlet loads applied in our experiment. In the treatment of odorous emissions, the inlet odorant concentrations are very low (in the order of μg m^{-3}-mg m^{-3}), and removal efficiency rather than elimination capacity is employed as process performance parameter. Therefore, the ECs obtained during odour treatment are not comparable to those obtained during the treatment of industrial VOC emissions, which is conducted at inlet VOC concentrations in the range of g m^{-3} (3-6 orders of magnitude higher than those found in odorous emissions). Since our study was devised to represent the concentrations typically found in odorous emissions, low inlet concentrations were employed for the VOCs (4.9 ± 0.5, 0.82 ± 0.07, 0.91 ± 0.10 and 0.75 ± 0.08 mg m^{-3} for MeSH, toluene, alpha-pinene and hexane, respectively). Nevertheless, a brief discussion, together with the maximum ECs recorded in the three bioreactors, were included in the revised version of the manuscript in accordance to Reviewer 3 suggestion (current page 15, lines 328-335): "Comparable maximum elimination capacities were recorded in the BF and BTF for MeSH (~1.2 g m^{-3} h^{-1}), toluene (~0.22 g m^{-3} h^{-1}), alpha-pinene (~0.25 g m^{-3} h^{-1}), and hexane (~0.20 g m^{-3} h^{-1}), while lower values (0.58, 0.11, 0.12 and 0.09 g m^{-3} h^{-1} for MeSH, toluene, alpha-pinene and hexane, respectively) were achieved in the HF-MBR. It is important to highlight that these elimination capacities were much lower than those reported in literature, since most VOC treatment studies are commonly conducted at inlet concentrations typically found in industrial emissions (which are ~3-6 orders of magnitude higher than those measured in odorous emissions)".

- in lines 419- 423, does this strong increased RE can be explained by the increased gradient due to consumption on the biofilm side? There may be also a change in the partition coefficient due to the biofilm.

The increased REs recorded in the membrane bioreactor compared to the transfer efficiency measured under abiotic conditions were here attributed to a higher concentration gradient as a result of VOC consumption within the biofilm. The authors agree with Reviewer 3 on the fact that this increase in RE could be also due to a variation in the partition coefficients mediated by the presence of the biofilm. An explanatory remark was included in the revised version of the manuscript to include this hypothesis (current page 19, lines 435-437): "…the formation of a biofilm increased the concentration gradients of the pollutants through the membrane due to a rapid VOC consumption on the biofilm side as observed during biotic operation…" and (current page 19, lines 441-443): "The presence of the biofilm could have also mediated a variation in the partition coefficient of the target VOCs, thus increasing their mass transport efficiency".

- Increased fungal content may be also due to hexane and a-pinene (line 440)

The mentioned increase in fungal content was observed by Prenafeta-Boldú et al. (2012) in a biofilter treating toluene. However, the authors agree with Reviewer 3 on the fact that in our

particular case the proliferation of fungi might be also due to the presence of hexane and alpha-pinene.

- I strongly suggest that table 1 be reduced to contain only the most relevant data and the whole table submitted as supplement data.

Table 1 was reduced and only one close relative to each band (Blast search) is now provided. Table 1 is now submitted as supplementary data as suggested by Reviewer 3 (current page 17, line 376): "The closest matches for every band (BLASTN) according to the NCBI database, together with its similarity percentages and sources of origin, are provided as supplementary material (Table 1)".

- Figure 4d) requires explanation

The authors apologize for this mistake. The corresponding figure caption was modified for clarification purposes and a detailed explanation of figure 4D was included in this revised version of the manuscript (current page 29, lines 639-646): "**Fig. 4.** Time course of the pressure drop in the biofilter (♦, A), the biotrickling filter (□, B) and the membrane bioreactor (○, C). Dashed vertical lines represent the changes in EBRT, the continuous vertical line in figure 4A the change in the biofilter irrigation rate and the vertical dotted arrows in figure 4C the membrane cleanings. Figure 4D represents the compression energy requirements in the biofilter (♦, dashed line), the compression and pumping energy requirements in the biotrickling filter (□, dotted line) and the membrane bioreactor (○, no line), and the maximum compression energy requirements (continuous line) at different EBRTs".

We hope that these modifications will comply with the request of the reviewers. Please do not hesitate to contact us at your convenience if you need further information.

Valladolid, 27 September 2013

Raúl Muñoz Raquel Lebrero

Comparative assessment of a biofilter, a biotrickling filter and a hollow fiber membrane bioreactor for odour treatment in wastewater treatment plants

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Abstract

A low abatement efficiency for the hydrophobic fraction of odorous emissions and a high footprint are often pointed out as the major drawbacks of conventional biotechnologies for odour treatment. In this work, two conventional biotechnologies (a compost-based biofilter, BF, and a biotrickling filter, BTF), and a hollow-fiber membrane bioreactor (HF-MBR) were comparatively evaluated in terms of odour abatement potential and pressure drop (ΔP) at empty bed residence times (EBRTs) ranging from 4 to 84 s, during the treatment of methyl-mercaptan, toluene, alpha-pinene and hexane at trace level concentrations (0.75 - 4.9 mg m^{-3}). High removal efficiencies (RE > 90% regardless of the air pollutant) were recorded in the BF at EBRTs ≥ 8 s, although the high ΔP across the packed bed limited its cost-effective operation to EBRTs > 19 s. A complete methyl-mercaptan, toluene and alpha-pinene removal was recorded in the BTF at EBRTs ≥ 4 s and ΔP lower than 33 mmH_2O (~611 Pa m_{bed}^{-1}), whereas slightly lower REs were observed for hexane (~88%). The HF-MBR completely removed methyl-mercaptan and toluene at all EBRTs tested, but exhibited an unstable alpha-pinene removal performance as a result of biomass accumulation and a low hexane abatement efficiency. Thus, a periodical membrane-cleaning procedure was required to ensure a steady abatement performance. Finally, a high bacterial diversity was observed in the three bioreactors in spite of the low carbon source spectrum present in the air emission.

Keywords: Biofilter; biotrickling filter; membrane bioreactor; odour treatment; volatile organic compounds.

1. Introduction

The increasing public expectations on air quality and the stricter environmental legislations concerning atmospheric pollution have resulted in a need for minimization and treatment of off-gas emissions. Malodours emitted from a wide variety of sources (wastewater treatment, landfilling and composting, meat rendering, petrochemical refining, food processing, pulp and paper manufacturing, etc.) are not only a direct threat for human health and wellbeing, but also contribute to photochemical smog formation and particulate secondary contaminant emission (Capelli et al., 2008; Shareefdeen et al., 2002; Sucker et al., 2008). These malodorous emissions are complex mixtures of odorants including sulfur derived and volatile organic compounds (VOCs) at low concentrations (μg m^{-3}-mg m^{-3}) compared to those emitted from industrial processes, and comprise large volumes of air released from widespread common facilities. These characteristics differentiate malodorous from industrial emissions and hinder their cost-efficient abatement.

Biotechnologies are nowadays recognized as the best available technologies for odour treatment due to their lower environmental impact and operating costs compared to their physical-chemical counterparts (Estrada et al., 2012). Among conventional biotechnologies, biofiltration and biotrickling filtration are by far the most commonly implemented technologies for odour abatement likely due to their ease of operation and the extensive design and operation experience (Iranpour et al., 2005; Kraakman et al., 2011). However, these biotechnologies are claimed to support low removal efficiencies for the hydrophobic fraction of malodorous emissions, whose elimination is mandatory for an efficient odour abatement (Iranpour et al., 2005; Liu et al., 2009). Typically, the presence of a water layer over the biofilm attached onto the packing material in biofilters and biotrickling filters limits the mass transfer of the most hydrophobic VOCs

61 from the gaseous phase to the aqueous biofilm (Kraakman et al., 2011). Therefore,
62 operation under non-mass transfer limiting conditions in these packed bioreactors
63 requires process design at high gas residence times, resulting in prohibitive land
64 requirements. Thus, new bioreactor configurations must be developed to guarantee a
65 cost-effective treatment of the hydrophobic fraction of the odorous emissions without
66 increasing the energy and/or cost to overcome the mass transfer limitation.

67 Advanced membrane bioreactors (AMBR) are based on a membrane-mediated
68 separation between the polluted air emission circulating through one side (from where
69 pollutants are transferred) and the microbial community attached on the other side of the
70 membrane and in contact with an aqueous phase containing the nutrients required for
71 microbial growth (Kumar et al., 2008). In this particular bioreactor configuration, the
72 presence of the membrane provides a selective extraction of the target pollutants and
73 oxygen, while the presence of a biofilm or a culture in suspension increases the local
74 concentration gradients of the pollutants degraded by the microorganisms. Both
75 mechanisms will theoretically enhance the mass transfer of the less water soluble
76 odorants and support a more efficient odour abatement performance than those achieved
77 by its biological counterparts (Semmens 2008). However, the implementation of AMBR
78 for off-gas treatment is very recent and the few studies conducted to date mainly
79 focused on the removal of single pollutants at higher concentrations (mg m^{-3} – g m^{-3}),
80 which does not support a direct extrapolation of the performance of AMBRs to the
81 treatment of odorous emissions (Kumar et al., 2008).

82 The present work aims at systematically comparing two conventional biotechnologies
83 (i.e. a biofilter (BF) and a biotrickling filter (BTF)) and a hollow-fiber membrane
84 bioreactor (HF-MBR) for odour treatment in terms of abatement efficiency and energy

consumption (pressure drop) under comparable operating conditions in a wide range of empty bed residence times (EBRTs).

2. Materials and methods

2.1 Microorganisms and culture conditions

Aerobic activated sludge collected at Valladolid wastewater treatment plant (Spain) was used as inoculum in all bioreactors evaluated. A SO_4^{2-} free mineral salt medium (MSM) was used for BF irrigation and as nutrient recycling solution in the BTF and the HF-MBR (Lebrero et al., 2011).

2.2 Experimental set-up

The experimental set-up consisted of a BF, a BTF and a HF-MBR operating in parallel (Fig. 1). Both the BF and the BTF were jacketed PVC columns with a working volume of 2 L (internal diameter = 0.083 m, height = 0.53 m). The BF was packed with compost (Pindstrup Mosebrug SAE, Spain) and the BTF with 1 cm^3 polyurethane foam cubes (Filtren TM 25280, Recticel Iberica, S.L.). The packing material was characterized according to standard methods (TMECC, 2002). The HF-MBR was a commercial hollow-fiber module (PermSelect® PDMSXA-8300 cm^2 module, MedArray Inc., USA) with a total module volume of 300 mL. The membrane was made of PDMS (silicone) and consisted of 10600 fibers (internal diameter = 190 µm, wall thickness = 55 µm) with a total membrane area of 8300 cm^2. The bioreactors were operated at a constant temperature of 25ºC.

The odorous stream was prepared by diluting a concentrated methyl-mercaptan (MeSH), toluene, alpha-pinene and hexane mixture from a calibration bottle (Abello

Linde S.A., Spain) with a humidified VOC-free air stream. The odorous stream was then equally split using mass flow controllers (Aalborg, USA) and fed to the BF, the BTF and the HF-MBR from the bottom of the reactors in a counter current configuration at concentrations of 4.9 ± 0.5, 0.82 ± 0.07, 0.91 ± 0.10 and 0.75 ± 0.08 mg m^{-3} for MeSH, toluene, alpha-pinene and hexane, respectively. The BF was periodically irrigated at 15 mL of MSM $L_{packing}^{-1}$ d^{-1} for the first 58 days of operation and at 60 mL of MSM $L_{packing}^{-1}$ d^{-1} from day 58 onwards. The recycling solution of the BTF and the HF-MBR was continuously agitated in two external 1-L tanks and recycled at a rate of 1.5 m h^{-1} and 15.5 mL m^{-2} min^{-1} (corresponding to 200 mL min^{-1}), respectively. The pH of both recycling solutions was manually controlled at ~7 by daily addition of a 10 g L^{-1} NaOH solution.

2.3 Abiotic VOC mass transfer characterization of the HF-MBR

The abiotic mass transport of the four target VOCs was characterized according to Kumar et al. (2009) at EBRTs ranging from 7 to 60 s under two different scenarios. First, clean air was supplied through the lumen of the HF-MBR, while the simulated odorous stream at inlet MeSH, toluene, alpha-pinene and hexane concentrations of 3.5 ± 0.6, 0.57 ± 0.02, 0.68 ± 0.11 and 0.66 ± 0.02 mg m^{-3}, respectively, circulated inside the fibers (air/air scenario). The clean air flow rate was set constant at 200 mL min^{-1} regardless of the EBRT tested. The inlet and outlet VOC concentrations in the simulated odorous stream and the outlet concentration in the clean air were periodically measured until the standard deviation of three consecutive measurements was lower than 10%, and the VOC mass balance over the reactor was evaluated to ensure the accuracy of the results obtained. The experiment was repeated by circulating MSM at 200 mL min^{-1} instead of clean air through the lumen of the HF-MBR (air/liquid scenario).

2.4 Operating procedure

Prior to process start-up, an abiotic test was conducted to assess any potential odorant removal due to adsorption or photolysis in the experimental set-up. The inlet and outlet VOC concentrations were periodically monitored for 5 days at an EBRT of 1 min in the absence of microbial activity (before inoculation and BF packing with compost).

The bioreactors were inoculated with 250 mL of activated sludge previously centrifuged at 10000 rpm for 10 min and resuspended in MSM at a concentration of 6.8 g L^{-1}. The influence of the EBRT on the odorant removal efficiency (RE) in the BF and BTF was evaluated at 48, 18 and 8 s. At day 78 (EBRT of 8 s), the packing material of the BF was removed and half of the compost was mixed with Kaldnes K1 plastic rings (polyethylene, diameter = 0.9 cm, surface area = 500 m^2 m^{-3}, Evolution Aqua Ltd., UK) due to the high pressure drop (ΔP) recorded in this bioreactor. At day 95 the BF was stopped, while the EBRT of the BTF was further decreased to 4 s for 22 days. The removal performance of the HF-MBR was evaluated at similar EBRTs (43, 34 and 16 s, calculated using the total volume of the membrane module) for 95 days. Several membrane cleanings were performed at days 21, 39, 72, and 102 in order to overcome biomass clogging by increasing the liquid recycling rate, which promoted biofilm sloughing due to the increased shear forces. This procedure was successfully implemented in previous studies (Lebrero et al. 2013, Studer 2005). However, due to the unstable and low VOC abatement performance recorded in this system, the EBRT was increased to 84 s in the last operating period.

The gas concentration of the VOCs was daily measured at both inlet and outlet sampling ports of each bioreactor. Liquid samples of 20 mL were periodically

withdrawn from the recycling liquid in the BTF and HF-MBR, replaced with MSM and filtered through a 0.22 μm filter in order to monitor the pH and the concentration of sulfate, dissolved total organic carbon (DOC), dissolved inorganic carbon (DIC) and dissolved total nitrogen (DTN). Distilled water was daily supplied to the systems to replace water losses by evaporation. Likewise, the ΔP in the three bioreactors and the temperature and moisture content in the inlet odorous emission were periodically recorded.

2.5 Analytical procedures

Gas samples for the analysis of the target odorants were collected in 250 mL glass bulbs (Sigma-Aldrich) and pre-concentrated for 10 min using 85 μm PDMS/Carboxen SPME fibers (Supelco, Bellefonte, USA). The SPME fibers were injected in a GC-FID (Varian 3900) equipped with a SupelcoWax (15 m×0.25 mm×0.25 μm) capillary column. Oven, injector and detector temperatures were maintained at 40, 300 and 300 ºC, respectively. The flowrates of H_2 and air were fixed at 30 and 300 mL min^{-1}, N_2 being used as the carrier gas at 1 mL min^{-1} and make-up gas at 25 mL min^{-1}. The pH of the recycling media was measured using a pH/mV/°C meter (pH 510 Eutech Instruments, Nijkerk, the Netherlands). Sulfate concentration was determined by HPLC-IC using an IC-Pak Anion HC (150 mm × 4.6 mm). DOC, DIC and DTN were measured using a TOC-VCSH analyzer (Shimadzu, Tokyo, Japan) coupled with a total nitrogen chemiluminesce detection module (TNM-1, Shimadzu, Japan). The moisture content and temperature in the influent odorous stream was recorded using a Testo 605-H1 thermohygrometer (Testo AG, Germany), and the ΔP in the bioreactors was determined by means of a differential pressure meter using water as the manometric fluid.

The compression energy requirements at each EBRT were calculated using the following expression to obtain the power requirements (P, W):

$$P = \frac{F \times \Delta P}{0.7}$$

Where F corresponds to the volumetric gas flow rate at each EBRT ($m^3\ s^{-1}$) and ΔP to the pressure drop measured across the packing media at the corresponding EBRT (Pa m_{bed}^{-1}). A standard blower efficiency of 0.7 was considered (Estrada et al., 2012). The liquid pumping costs were also calculated for the BTF and the HF-MBR assuming a constant pressure drop for the liquid of 1 bar.

2.6 Microbiological procedures

In order to evaluate the richness and composition of the bacterial communities present in the bioreactors, biomass samples of the inocula (both fresh activated sludge (1) and activated sludge after mixing with compost (2)) and biomass samples collected from the bioreactors at the end of their operation (BF (3), BTF (4), HF-MBR recycling liquid (5) and HF-MBR biofilm (6)) were collected and stored immediately at – 20ºC. The genomic DNA was extracted according to Lebrero et al. (2012). The PCR mixture (50 µL) was composed of 25 µL of BIOMIX ready-to-use 2× reaction mix (Bioline, Ecogen) containing reaction buffer, magnesium, deoxynucleotide triphosphates (dNTPs), Taq polymerase and additives, l or 2 µL of the extracted DNA, PCR primers 968-F-GC and 1401-R (10µM) (Sigma- Aldrich, St. Louis,MO, USA) for bacterial 16S rRNA gene amplification, and Milli-Q water up to a final volume of 50 µL. The PCR thermo-cycling program used was previously described in Lebrero et al. (2012). The DGGE analysis of the amplicons was performed with a D-Code Universal Mutation

Detection System (Bio Rad Laboratories) using 8% (w/v) polyacrylamide gel with a urea/formamide denaturing gradient from 45 to 65%. The DGGE running conditions were applied according to Roest et al. (2005). The gels were stained with GelRed Nucleic Acid Gel Stain (biotium) for 1 h and the obtained DGGE patterns processed using the GelCompar IITM software (Applied Maths BVBA, Sint-Martens-Latem, Belgium). After image normalization, bands were defined for each sample using the bands search algorithm within the program. Similarity indices of the compared profiles were calculated from the densitometric curves of the scanned DGGE profiles by using the Pearson product–moment correlation coefficient (Häne et al., 1993). The peak heights in the densitometric curves were also used to determine the Shannon–Wiener diversity index (H), which considered both the relative number of the DGGE bands (richness) and their relative intensities (evenness):

$$H = -\sum \left[P_i \ln(P_i) \right]$$

where P_i is the importance probability of the bands in a lane ($P_i = n_i/n$, where n_i is the height of an individual peak and n is the sum of all peak heights in the densitometric curves).

Sequencing and DNA sequence analysis

Selected bands were excised from the DGGE gel in order to identify the bacteria present in the samples above described. The procedure was previously described in Lebrero et al. (2011). The taxonomic position of the sequenced DGGE bands was obtained using the RDP classifier tool (50% confidence level) (Wang et al., 2007). The closest matches to each band were obtained using the BLAST search tool at the NCBI (National Centre

for Biotechnology Information) (McGinnis and Madden, 2004). Sequences were deposited in GenBank Data Library under accession numbers KF112977- KF112995.

3. Results

3.1 Packing material characterization

Polyurethane foam presented a notably lower density and wet bed density (0.01 and 0.30 g mL^{-1}, respectively) than compost (0.23 and 0.87 g mL^{-1}, respectively), but a ~25% higher porosity (96% vs. 72%). Conversely, its water retention capacity (0.12 L_{water} $L_{polyurethane}^{-1}$) was significantly lower than that of compost (0.68 L_{water} $L_{compost}^{-1}$). Finally, the pH of compost was slightly acidic (5.3) and lower than that recorded for polyurethane foam (6.3).

3.2 Abiotic VOC mass transfer characterization of the HF-MBR

When air circulated in both sides of the membrane, the four VOCs were equally transported regardless of their hydrophobicity and size, the transport efficiency increasing linearly with the gas residence time (Fig. 2A). Low mass transport efficiencies (5 - 8%) were observed at 7 s of EBRT, increasing to ~17% and 31% at 16 and 30 s, respectively, regardless of the odorant. At 45 s, the transport through the membrane increased to 48-54% for all VOCs. Maximum mass transport efficiencies were observed for hexane at 60 s of EBRT (65%), while slightly lower values were recorded for toluene and MeSH (62%), and alpha-pinene (57%). Under the gas/liquid scenario, the mass transfer of the soluble VOCs noticeably increased compared to the air/air scenario, while the presence of the aqueous phase significantly hindered the

transport of the more hydrophobic VOCs (Fig. 2B). Thus, MeSH was almost completely transferred to the liquid phase (>90%) at EBRTs higher than 16 s, its transport decreasing to 77% at an EBRT = 7 s. Toluene transfer efficiencies > 92% were also achieved at EBRTs > 45 s, with lower values recorded at 30 s (84%), 16 s (66%) and 7 s (43%). Similarly, 88% of alpha-pinene was transferred at an EBRT of 60 s, while at 7 s only 41% of this terpene passed through the membrane. Finally, the mass transfer efficiency of hexane decreased from 18% to 6% when decreasing the EBRT from 60 to 7 s, respectively.

3.3 Influence of the EBRT on the removal performance and pressure drop

Steady state MeSH (Fig. 3A), toluene (Fig. 3B) and alpha-pinene (Fig. 3C) removal efficiencies (REs) were rapidly achieved in the BF after inoculation (2-4 days), while 8 days were necessary for hexane RE stabilization (Fig. 3D). Following this rapid start-up, steady MeSH, toluene and alpha-pinene REs > 99% and hexane RE of 97.7 ± 0.8% were recorded at an EBRT of 43 s. During this first period, the ΔP remained always < 4 mmH_2O, increasing to ~50 mmH_2O by day 28 (Fig. 4A). The subsequent decrease in EBRT to 18 s (EBRT significantly lower than those typically used in biofiltration of 60-120 s) did not affect the VOC abatement performance. Hence, although the BF was able to maintain MeSH, toluene and alpha-pinene REs > 98% and slightly lower hexane REs (96.1±1.9%), the decrease in EBRT resulted in an additional increase in ΔP to 186 ± 10 mmH_2O. A further reduction in the EBRT to 8 s caused an initial deterioration in the removal capacity of the biofilter by day 57 concomitant with a ΔP increase up to 502 ± 21 mmH_2O and a gradual drying of the packing material. Therefore, the irrigation frequency was increased by day 58, which mediated a rapid restoration of the previous

VOC removal performances together with a dramatic increase in the ΔP to values > 2 mH_2O by day 77. In order to decrease the ΔP, half of the compost of the BF packing material was replaced by plastic rings by day 78. A subsequent deterioration of the toluene and hexane REs was observed followed by performance stabilization at steady toluene RE of 98.0 ± 0.7% and hexane RE of 93.7 ± 0.7% after 3 and 10 days, respectively. On the other hand, MeSH and alpha-pinene REs were not affected by the packing replacement and steady values of 98.0 ± 1.5% and 98.8 ± 1.4% were maintained at an EBRT = 8 s. The renewal of the packing material resulted in an initial decrease in the ΔP to ~200 mmH_2O, although it rapidly increased again up to 1.3 mH_2O by day 94.

In the BTF, MeSH (Fig. 5A), toluene (Fig. 5B) and alpha-pinene (Fig. 5C) REs > 99% were achieved after 12, 5 and 8 days of acclimation, respectively, while steady hexane REs of 94.8 ± 1.7% were recorded 18 days after the start-up of the system (Fig. 5D). This significantly higher acclimation times compared to the BF were likely due to the lack of an inherent microbial diversity (as shown by the lower Shannon diversity index of the activated sludge without compost) and adsorption to organic matter as those present in the compost. The ΔP during this period did not exceed 5 mmH_2O (Fig. 4B). Likewise, MeSH, toluene and alpha-pinene REs > 99% and hexane RE of 91.8 ± 3.9% were maintained at an EBRT of 18 s. The ΔP values also increased up to 10 mmH_2O by day 51. At an EBRT of 8 s, MeSH and toluene were almost completely removed, while alpha-pinene RE slightly decreased to 98.6 ± 1.8%. A period of instability in the hexane removal performance was observed until day 79, followed by a performance stabilization at RE = 96.1 ± 2.2%. During this period, the ΔP fluctuated between 6 and 23 mmH_2O. By day 95 the EBRT was further deceased to 4 s, and steady REs > 97%

for MeSH, toluene and alpha-pinene were immediately achieved. On the other hand, hexane removal decreased to 88.4 ± 1.1% and steady ΔP of 29 ± 4 mmH_2O was recorded at the lowest EBRT.

After 10 days of operation, MeSH REs > 93% were recorded in the HF-MBR at 43, 34 and 16 s of EBRT (Fig. 6A). When the EBRT was increased to 84 s MeSH RE steadily decreased to a minimum value of 68.5% by day 101. Membrane cleaning at day 102 allowed for the recovery of MeSH removal, which finally stabilized at 98.4 ± 1.7%. Toluene RE fluctuated between 66.8% and 99.0% when the HF-MBR was operated at an EBRT of 43 s (Fig. 6B). When the EBRT was decreased to 34 and 16 s, toluene removal stabilized at ~96.0%. By day 95, at an EBRT of 84 s, toluene RE suddenly decreased to minimum values of 72.4%, increasing to 97.6 ± 2.4% after membrane cleaning. A stable alpha-pinene abatement was not achieved regardless of the EBRT (Fig. 6C). Initially, alpha-pinene RE increased gradually up to 96.7%, but decreased subsequently to RE of 69.7% by day 20. After membrane cleaning at day 21, the alpha-pinene removal progressively increased to 94.8%. Three additional membrane cleanings were performed due to periodic deteriorations in the MBR abatement performance, the alpha-pinene RE recovering subsequently and achieving values ranging from 80 to 99%. Finally, low hexane REs were recorded during the entire experimentation period (Fig. 6D). At an EBRT of 43 s, a maximum hexane RE of 58.4% was recorded by day 63. The RE decreased afterwards and remained constant at 38.3 ± 6.2% regardless of the membrane cleaning or the EBRT. The final increase in EBRT to 84 s did not change significantly the hexane removal performance, with steady values of 44.9 ± 2.5% recorded by the end of the experimentation period. Pressure drop values ranged between 42 and 159 mmH_2O at EBRTs of 43 and 34 s, decreasing to 9 mmH_2O after the second

membrane cleaning by day 39 (Fig. 4C). Increases in the ΔP were periodically recorded as a result of biomass accumulation (the highest value of 192 mmH_2O was achieved at an EBRT of 84 s), gradually recovering previous values after each membrane cleaning.

Comparable maximum elimination capacities were recorded in the BF and BTF for MeSH (~1.2 g m^{-3} h^{-1}), toluene (~0.22 g m^{-3} h^{-1}), alpha-pinene (~0.25 g m^{-3} h^{-1}), and hexane (~0.20 g m^{-3} h^{-1}), while lower values (0.58, 0.11, 0.12 and 0.09 g m^{-3} h^{-1} for MeSH, toluene, alpha-pinene and hexane, respectively) were achieved in the HF-MBR. It is important to highlight that these elimination capacities were much lower than those reported in literature, since most VOC treatment studies are commonly conducted at inlet concentrations typically found in industrial emissions (which are ~3-6 orders of magnitude higher than those measured in odorous emissions).

Liquid samples from the BF were only taken during the first 30 days of experimentation due to the absence of leachate from that day on. During that period, a decrease in the pH from 4.7 to 4.2 was recorded. DOC and DTN values ranging from 91 to 370 mg L^{-1} and from 460 to 770 mg L^{-1}, respectively, and sulphate concentration of 1569 ± 28 mg L^{-1} were recorded during that period. Sulphate production clearly confirmed the mineralization of MeSH, since a sulphate-free MSM was employed. In the BTF recycling liquid, the DOC remained stable at 47.2 ± 7.2 mg L^{-1}, while the DTN initially increased from 170 up to 287 mg L^{-1} by day 21 probably due to water evaporation, stabilizing afterwards at ~269 ± 14 mg L^{-1} until day 54 and decreasing again to stable values of 144 ± 19 mg L^{-1}. The pH remained stable at 6.85 ± 0.17 in this recycling medium during the complete experimentation period, while sulphate concentration

348 increased from 245 to 3532 mg L^{-1} by day 117. Finally, the DOC steadily decreased
349 from initial values of 35 to ~5 mg L^{-1} by day 103 in the HF-MBR, whereas the DTN
350 remained stable at 171 ± 29 mg L^{-1}. The pH in the MBR recycling medium was
351 maintained at 6.92 ± 0.20 and the sulphate concentration was always <5 mg L^{-1},
352 sporadically increasing up to 340 mg L^{-1}. In this particular bioreactor, it is not possible
353 to ascertain sulphate accumulation in the recycling liquid due to the frequent membrane
354 cleaning, which were accompanied by a significant media replacement.

355

356 **3.4 Bacterial population dynamics**

357 The Shannon-Wiener diversity index takes into account both the number (richness) and
358 the evenness of the species, typical values ranging from 1.5 to 3.5 (low and high species
359 evenness and richness, respectively) (McDonald 2003). All samples exhibited high
360 diversity indices (3.2 - 3.5) except for sample 3 (end of BF operation), which presented
361 a slightly lower diversity index of 2.8 (Fig. 7). The analysis of the Pearson similarity
362 coefficients showed a high similarity between the activated sludge inoculum and both
363 the microbial community present in the BTF at the end of the experiment (samples 1
364 and 4 = 69.1%) and the recycling liquid of the HF-MBR (samples 1 and 5 = 70.5%). In
365 addition, the bacterial community initially present in the activated sludge mixed with
366 the compost exhibited a 72% similarity with the final communities present in the BF
367 (samples 2 and 3 = 72%). The final composition of the microbial community
368 established in the BF noticeably differed from the community in the BTF (48.9%) or in
369 the HF-MBR (44.2%). Finally, the samples retrieved from the recycling liquid and the
370 biofilm in the HF-MBR exhibited a high similarity (79.9%).

From the DGGE gel, 19 bands were sequenced (Fig. 7) and 6 different phyla were retrieved in the RDP database: *Proteobacteria* (8 bands), *Actinobacteria* (3 bands), *Nitrospira* (2 bands), *Verrucomicrobia* (2 bands), *Acidobacteria* (1 band) and *Chlamydiae* (1 band), while two bands remained unclassified. The closest matches for every band (BLASTN) according to the NCBI database, together with its similarity percentages and sources of origin, are provided as supplementary material (Table 1).

4. Discussion

High REs were recorded in the BF for all the VOCs evaluated, including hexane (the most hydrophobic VOC), even at an EBRT of 8 s. However, the operation at low EBRTs and the progressive deterioration of the packing material (loss of compost structure and compaction) resulted in high pressure drops across the packed bed ($\Delta P >$ 14800 Pa m_{bed}^{-1}). The analysis of the compression energy requirements and its comparison with the recommended maximum cost-effective compression energy needs (calculated from a maximum cost-effective value of ΔP of 1500 Pa m_{bed}^{-1}, Estrada et al., 2012) clearly showed that the operation of the compost-BF at EBRTs lower than 19 s might compromise the economic viability of odour abatement (Fig. 4D). Indeed, the development of high ΔP in compost-based BFs within a short operation period has been frequently reported in the literature: Dorado et al. (2012) observed ΔP of 2000 Pa m_{bed}^{-1} in a BF packed with compost-covered clay pellets, while Estrada et al. (2013) recorded ΔP over 4000 Pa m_{bed}^{-1} after 32 days of operation of a compost-based biofilter. Thus, in spite of the advantages of this packing material (a high diversity of indigenous microbial species, high nutrient content, good water retention and porosity, low cost and availability), its poor structural stability often entails a reduced bed lifespan. Consequently, a stable and efficient removal of a wide hydrophobicity range of odorants

396 can be achieved in biofilters when properly operated, while energy requirements often
397 result in process operation at high EBRTs with a frequent media replacement.
398
399 In terms of process economics and land requirements, BTFs overcome BFs due to their
400 high VOC removal performance and low ΔP at EBRTs as low as 4 s. In this context,
401 high REs have been reported in literature for H_2S, MeSH and toluene in laboratory and
402 field scale BTFs at a wide range of EBRTs (ranging from 5 to 60 s) (Patria et al., 2001;
403 Ramirez et al., 2009; Yang et al., 2011). In our particular study, the continuous
404 recycling of the aqueous nutrient solution entailed slightly lower REs for the most
405 hydrophobic VOCs at the low gas residence times tested as a result of mass transfer
406 limitations (~88% hexane removal). Moreover, even at the low EBRTs applied in BTFs,
407 the high flow rates of odorous emissions to be treated still result in large bioreactor
408 footprints, hindering their implementation in facilities with space limitations.
409
410 In this regard, membrane bioreactors are compact systems capable of providing higher
411 specific surface areas in lower reactor volumes, which constitutes the main advantage of
412 this configuration. Previous studies demonstrated the feasibility of applying membrane
413 bioreactors for treating individual industrial VOCs from waste gas emissions, although
414 biomass accumulation and clogging is still an important drawback to be solved
415 (Attaway et al., 2001; Álvarez-Hornos et al., 2011). Traditionally, biomass plugging
416 was only attributed to microporous or composite membranes due to the blockage of the
417 membrane pores by the biofilm (Attaway et al., 2002). However, an excessive biomass
418 growth also deteriorated the VOC abatement performance of the dense silicone
419 membrane tested in our experimental set-up. It was hypothesized that the accumulation

420 of biomass in the MBR lumen increased the pressure of the recycling liquid, which
421 compressed the thin silicone tubes, decreasing the cross sectional area and subsequently
422 reducing the actual gas residence time and increasing the ΔP of the odorous emission. In
423 addition, the formation of a thick biofilm on the membrane created an additional mass
424 transfer resistance, which likely resulted in a deterioration of the membrane
425 performance. This phenomenon was more evident for alpha-pinene, whose RE
426 significantly decreased due to membrane clogging and increased subsequently to each
427 membrane cleaning. On the other hand, dense PDMS membranes are reported to offer
428 higher and constant REs, together with a high permeability for the hydrophobic
429 compounds (Kumar et al., 2008). In our particular case, the abiotic study did not show
430 any difference between the mass transport efficiency of the 4 target VOCs in the air/air
431 scenario, while hexane mass transport efficiency was the lowest in the air/liquid
432 scenario. In this context, some authors have reported how the sorption and diffusivity
433 across the membrane of one component can be modified due to the interactions with
434 other components (Kraakman et al., 2007). Nevertheless, and in spite of the low
435 transport efficiencies observed under the air/liquid scenario, the formation of a biofilm
436 increased the concentration gradients of the pollutants through the membrane due to a
437 rapid VOC consumption on the biofilm side as observed during biotic operation. For
438 instance, while only 11% of hexane was transported through the membrane under the
439 air/liquid scenario, an average RE of 38.3% was recorded under biotic operation.
440 Similarly, both MeSH and toluene exhibited an improved biotic mass transport
441 regardless of the EBRT tested. The presence of the biofilm could have also mediated a
442 variation in the partition coefficient of the target VOCs thus increasing their mass
443 transport efficiency. The MBR configuration could have also played an important role
444 in the results here obtained, since although HF-MBRs offer higher specific gas-liquid

surface areas (~2700 m^2 m^{-3}), flat sheet configurations are easier to operate in terms of membrane cleaning and replacement (Ergas and McGrath 1997). Thus, although membrane bioreactors constitute a promising alternative for treating gaseous emissions containing soluble and moderately soluble VOCs such as MeSH, toluene or alpha-pinene when clogging problems are overcome, the potential performance enhancement for the removal of hydrophobic compounds was not observed. At this point, it is important to remark that the actual residence time of the membrane bioreactor (calculated as the real volume available for gas circulation divided by the gas flow rate) is much lower compared to those of the BF and the BTF. In this sense, the EBRT must be multiplied by 0.72, 0.96 and 0.14 (void volume of the BF, the BTF and the HF-MBR, respectively) in order to obtain the actual gas residence time in each bioreactor. The low gas residence time in the HF-MBR could have mediated the lower hexane removal performances recorded in this system.

A highly diverse bacterial community was present in the three bioreactors, even under the low VOC mass loadings applied, an empirical finding also observed in bioreactors treating low odorant concentrations (Friedrich et al., 2002; Lebrero et al., 2011). The maintenance of a high microbial diversity in the process is a key issue to ensure an efficient and stable long term bioreactor operation. The lowest bacterial diversity (H=2.8) was recorded in the BF after 95 days of operation, in spite of the higher diversity of the BF inoculum (mixture of activated sludge and compost). This decrease in diversity could be attributed to the proliferation of fungi and the subsequent increase in the fungal/bacteria ratio likely mediated by pH decrease or excessive salt accumulation in the packing material, but the presence of fungi was not analyzed in this

469 study. The increase in the fungal biomass during the operation of organic-packed BFs
470 has been previously reported by Prenafeta-Boldú et al. (2012) in a BF treating toluene.

471

472 Microorganisms potentially capable of degrading MeSH and VOCs were detected in
473 this work. Species from the phylum *Proteobacteria* were retrieved in all samples:
474 *Xanthomondaceae*-like bacteria (fragments 2 and 3) and *Rhodanobacter*-like bacteria
475 have been previously detected in BFs, BTFs and membrane bioreactors treating odorous
476 exhaust air, the latter being able to degrade aromatic hydrocarbons (Kristiansen et al.,
477 2011; Lebrero et al., 2013). Fragment 6 was affiliated to the *Thiobacillus* genus, with a
478 99% of similarity to *Thiobacillus denitrificans* according to the BLAST analysis
479 (McGinnis and Madden 2004). This facultative anaerobic chemolithotroph is able to
480 couple the oxidation of inorganic sulfur compounds to the reduction of oxidized
481 nitrogen compounds (Beller et al., 2006). Different *Thiobacillus* bacteria were
482 previously found in BFs and BTFs treating MeSH and other sulphur odorants (Maestre
483 et al., 2010; Ramirez et al., 2009). Besides, *Alcaligenaceae* bacteria (fragment 7),
484 detected with a high intensity in the BTF and the HF-MBR biofilm, have shown a high
485 catabolic potential for aromatic compounds (Pérez-Pantoja et al., 2011). *Actinobacteria*,
486 which include aromatic and aliphatic degrading microorganisms, were also found in this
487 study (fragments 9, 10, 11), mostly in the inoculum samples. Bacteria from the Genus
488 *Gordonia* (fragment 9) within the Actinobacteria class, which have been previously
489 retrieved from a bioreactor co-treating H_2S and toluene, were also detected in the BF
490 and the HF-MBR samples with a high intensity (Gao et al., 2011). Several species
491 within the genus *Gordonia* exhibit the capacity to degrade aliphatic and aromatic
492 hydrocarbons while playing an important role in wastewater treatment bioreactors and
493 biofilters (Arenskötter et al., 2004). *Nitrospira* related organisms are among the most

494 diverse and widespread nitrifiers in natural ecosystems and biological wastewater
495 treatment. Microorganisms within the *Nitrospira* phylum, which are able to degrade
496 aromatic and non-aromatic hydrocarbons (Kristiansen et al., 2011; Lebrero et al., 2011),
497 were observed in all samples except in the BF (fragments 12 and 13). On the other
498 hand, microorganisms classified into the *Acidobacteria* phylum (fragment 16) were
499 found in the samples from the BTF and the HF-MBR. These bacteria have been also
500 retrieved from a BTF and a membrane bioreactor treating VOCs at trace level
501 concentrations (Lebrero et al., 2012; Lebrero et al., 2013). Fragments 18 and 19 were
502 unclassified bacteria predominantly found in the BTF (fragment 18) and the HF-MBR
503 (fragment 19). Finally, it is also worth noting the high similarity (~80%) observed
504 between the microbial population in the biofilm of the HF-MBR and in the recycling
505 suspended culture.

506

507 ## Conclusions

508 To the best of our knowledge, this work constitutes the first comparative study of a HF-
509 MBR and two conventional biotechnologies (BF and BTF) in terms of odorant
510 abatement capacity and energy requirements. The BTF was the most cost-effective
511 technology, offering a high VOC abatement at low EBRTs and pressure drops.
512 Conversely, the operation of the BF at low EBRTs entailed high pressure drops across
513 the bed, which in turn results in prohibitive operating costs. The HF-MBR provided a
514 good abatement performance for the soluble odorants, although unstable alpha-pinene
515 and low hexane removals were recorded in this bioreactor configuration, the low
516 performance of alpha-pinene being associated to membrane clogging due to biomass
517 overgrowth. Hence, the successful implementation of MBR for odour treatment still

518 requires further research on biofilm accumulation control to avoid operational problems
519 such as hindered pollutant diffusion or reactor clogging.

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628

Figure captions

Fig. 1. Schematic representation of the experimental set-up.

Fig. 2. Influence of the EBRT on the transport efficiency of MeSH (×), toluene (○), alpha-pinene (□) and hexane (♦) through the membrane in the air/air (A) and air/liquid (B) scenarios.

Fig. 3. Time course of the inlet (○) and outlet (+) concentrations, and removal efficiency (▲) in the biofilter for MeSH (A), toluene (B), alpha-pinene (C) and hexane (D). Vertical dashed lines represent the changes in EBRT, the vertical continuous line the change in the biofilter irrigation rate and the vertical dotted line the change of the biofilter packing material.

Fig. 4. Time course of the pressure drop in the biofilter (♦, A), the biotrickling filter (□, B) and the membrane bioreactor (○, C). Dashed vertical lines represent the changes in EBRT, the continuous vertical line in figure 4A the change in the biofilter irrigation rate and the vertical dotted arrows in figure 4C the membrane cleanings. Figure 4D represents the compression energy requirements in the biofilter (♦, dashed line), the compression and pumping energy requirements in the biotrickling filter (□, dotted line) and the membrane bioreactor (○, no line), and the maximum compression energy requirements (continuous line) at different EBRTs.

Fig. 5. Time course of the inlet (○) and outlet (+) concentrations, and removal efficiency (▲) in the biotrickling filter for MeSH (A), toluene (B), alpha-pinene (C) and hexane (D). Vertical dashed lines represent the changes in EBRT.

Fig. 6. Time course of the inlet (○) and outlet (+) concentrations, and removal efficiency (▲) in the hollow-fiber membrane bioreactor for MeSH (A), toluene (B),

652 alpha-pinene (C) and hexane (D). Vertical dashed lines represent the changes in EBRT
653 and the vertical continuous lines the membrane cleanings.

654 **Fig. 7.** Bacterial DGGE profiles. Sample names and Shannon diversity indices are
655 indicated in the upper part of the gel: (1) fresh activated sludge, (2) activated sludge
656 after mixing with compost, (3) BF, (4) BTF, (5) HF-MBR recycling liquid, and (6) HF-
657 MBR biofilm. The sequenced DGGE bands are indicated with an arrow (►) and the
658 corresponding number of each band.

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Research Highlights

- The biotrickling filter was the most cost-effective technology for odour treatment
- Operation of the biofilter at low residence times entails excessive operating costs
- The membrane bioreactor provided a good abatement for water soluble odorants
- Membrane clogging limited the abatement of alpha-pinene
- The reactors showed a high microbial diversity in spite of the low C source spectrum

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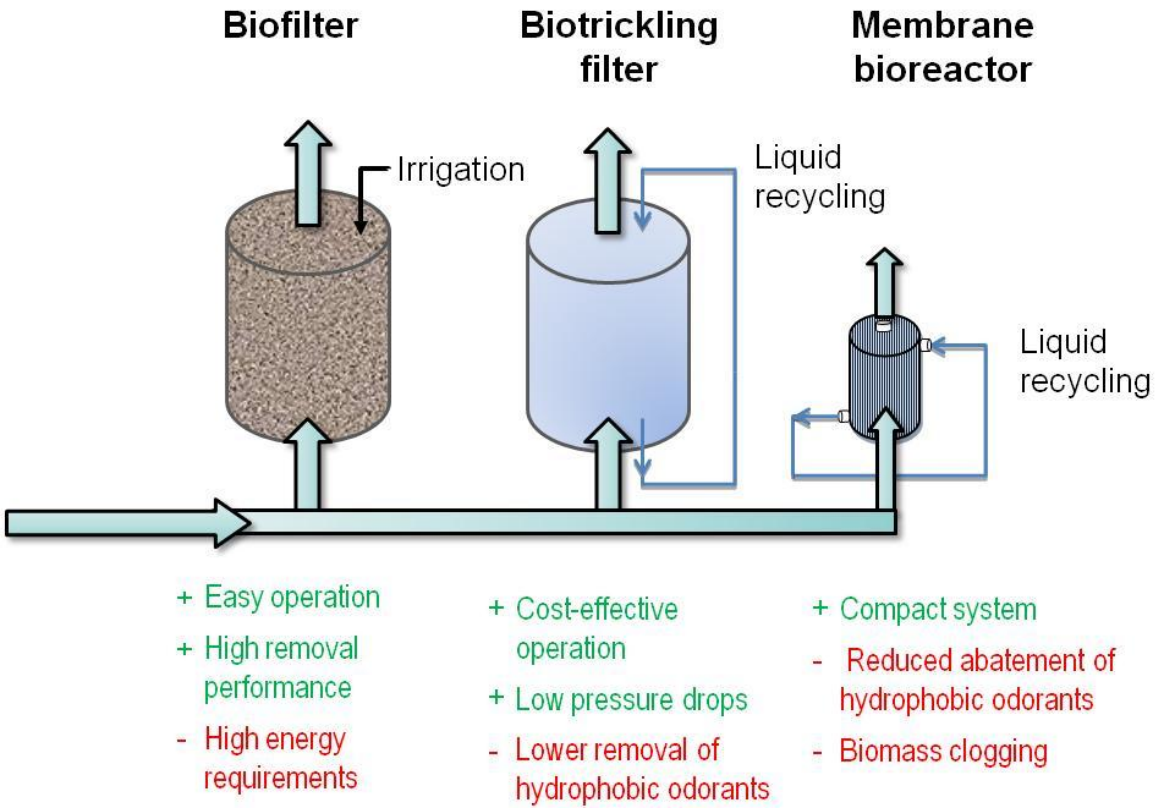
Graphical Abstract (for review)



Comparative assessment of a biofilter, a biotrickling filter and a hollow fiber membrane bioreactor for odour treatment in wastewater treatment plants

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Abstract

A low abatement efficiency for the hydrophobic fraction of odorous emissions and a high footprint are often pointed out as the major drawbacks of conventional biotechnologies for odour treatment. In this work, two conventional biotechnologies (a compost-based biofilter, BF, and a biotrickling filter, BTF), and a hollow-fiber membrane bioreactor (HF-MBR) were comparatively evaluated in terms of odour abatement potential and pressure drop (ΔP) at empty bed residence times (EBRTs) ranging from 4 to 84 s, during the treatment of methyl-mercaptan, toluene, alpha-pinene and hexane at trace level concentrations (0.75 - 4.9 mg m^{-3}). High removal efficiencies (RE > 90% regardless of the air pollutant) were recorded in the BF at EBRTs ≥ 8 s, although the high ΔP across the packed bed limited its cost-effective operation to EBRTs > 19 s. A complete methyl-mercaptan, toluene and alpha-pinene removal was recorded in the BTF at EBRTs ≥ 4 s and ΔP lower than 33 mmH_2O (~611 Pa m_{bed}^{-1}), whereas slightly lower REs were observed for hexane (~88%). The HF-MBR completely removed methyl-mercaptan and toluene at all EBRTs tested, but exhibited an unstable alpha-pinene removal performance as a result of biomass accumulation and a low hexane abatement efficiency. Thus, a periodical membrane-cleaning procedure was required to ensure a steady abatement performance. Finally, a high bacterial diversity was observed in the three bioreactors in spite of the low carbon source spectrum present in the air emission.

Keywords: Biofilter; biotrickling filter; membrane bioreactor; odour treatment; volatile organic compounds.

1. Introduction

The increasing public expectations on air quality and the stricter environmental legislations concerning atmospheric pollution have resulted in a need for minimization and treatment of off-gas emissions. Malodours emitted from wastewater treatment plants are not only a direct threat for human health and wellbeing, but also contribute to photochemical smog formation and particulate secondary contaminant emission (Sucker et al., 2008). These malodorous emissions are complex mixtures of odorants including sulfur derived and volatile organic compounds (VOCs) at low concentrations (μg m^{-3}-mg m^{-3}), which differentiate malodorous from industrial emissions and hinder their cost-efficient abatement.

Biotechnologies are nowadays recognized as the best available technologies for odour treatment due to their lower environmental impact and operating costs compared to their physical-chemical counterparts (Estrada et al. 2012). Among conventional biotechnologies, biofiltration and biotrickling filtration are by far the most commonly implemented technologies for odour abatement likely due to their ease of operation and the extensive design and operation experience (Iranpour et al. 2005, Kraakman et al. 2011). However, these biotechnologies are claimed to support low removal efficiencies for the hydrophobic fraction of malodorous emissions, whose elimination is mandatory for an efficient odour abatement (Iranpour et al. 2005, Liu et al. 2009). Typically, the presence of a water layer over the biofilm attached onto the packing material in biofilters and biotrickling filters limits the mass transfer of the most hydrophobic VOCs from the gaseous phase to the aqueous biofilm (Kraakman et al. 2011). Therefore, operation under non-mass transfer limiting conditions in these packed bioreactors requires process design at high gas residence times, resulting in prohibitive land requirements. Thus, new bioreactor configurations must be developed to guarantee a

cost-effective treatment of the hydrophobic fraction of the odorous emissions in wastewater treatment plants.

Advanced membrane bioreactors (AMBR) are based on a membrane-mediated separation between the polluted air emission circulating through one side and the microbial community attached on the other side of the membrane and in contact with an aqueous phase containing the nutrients required for microbial growth (Kumar et al. 2008). In this particular bioreactor configuration, the presence of the membrane provides a selective extraction of the target pollutants and oxygen, while the presence of a biofilm or a culture in suspension increases the local concentration gradients. Both mechanisms will theoretically enhance the mass transfer of the less water soluble odorants and support a more efficient odour abatement performance than those achieved by its biological counterparts (Semmens 2008). However, the implementation of AMBR for off-gas treatment is very recent and the few studies conducted to date mainly focused on the removal of single pollutants at higher concentrations (mg m^{-3} – g m^{-3}), which does not support a direct extrapolation of the performance of AMBRs to the treatment of odorous emissions (Kumar et al. 2008).

The present work aims at systematically comparing two conventional biotechnologies (i.e. a biofilter (BF) and a biotrickling filter (BTF)) and a hollow-fiber membrane bioreactor (HF-MBR) for odour treatment in terms of abatement efficiency and pressure drop under comparable operating conditions in a wide range of empty bed residence times (EBRTs).

2. Materials and methods

2.1 Microorganisms and culture conditions

Aerobic activated sludge collected at Valladolid wastewater treatment plant (Spain) was used as inoculum in all bioreactors evaluated. A SO_4^{2-} free mineral salt medium (MSM) was used for BF irrigation and as nutrient recycling solution in the BTF and the HF-MBR (Lebrero et al. 2011).

2.2 Experimental set-up

The experimental set-up consisted of a BF, a BTF and a HF-MBR operating in parallel (Fig. 1). Both the BF and the BTF were jacketed PVC columns with a working volume of 2 L (internal diameter = 0.083 m, height = 0.53 m). The BF was packed with compost (Pindstrup Mosebrug SAE, Spain) and the BTF with 1 cm^3 polyurethane foam cubes (Filtren TM 25280, Recticel Iberica, S.L.). The packing material was characterized according to standard methods (TMECC, 2002). The HF-MBR was a commercial hollow-fiber module (PermSelect® PDMSXA-8300 cm^2 module, MedArray Inc., USA) with a total volume of 300 mL. The bioreactors were operated at a constant temperature of 25ºC.

The odorous stream was prepared by diluting a concentrated methyl-mercaptan (MeSH), toluene, alpha-pinene and hexane mixture from a calibration bottle (Abello Linde S.A., Spain) with a humidified VOC-free air stream. The odorous stream was then equally split using mass flow controllers (Aalborg, USA) and fed to the BF, the BTF and the HF-MBR from the bottom of the reactors in a counter current configuration at concentrations of 4.9 ± 0.5, 0.82 ± 0.07, 0.91 ± 0.10 and 0.75 ± 0.08 mg m^{-3} for MeSH, toluene, alpha-pinene and hexane, respectively. The BF was periodically irrigated at 15 mL of MSM $L_{packing}^{-1}$ d^{-1} for the first 58 days of operation and at 60 mL of MSM $L_{packing}^{-1}$ d^{-1} from day 58 onwards. The recycling solution of the

BTF and the HF-MBR was continuously agitated in two external 1-L tanks and recycled at a rate of 1.5 m h^{-1} and 15.5 mL m^{-2} min^{-1} (corresponding to 200 mL min^{-1}), respectively. The pH of the trickling solution was manually controlled at ~7 by daily addition of a 10 g L^{-1} NaOH solution.

2.3 Abiotic VOC mass transfer characterization of the HF-MBR

The abiotic mass transport of the four target VOCs was characterized according to Kumar et al. (2009) at EBRTs ranging from 7 to 60 s under two different scenarios. First, clean air was supplied through the lumen of the HF-MBR, while the simulated odorous stream at inlet MeSH, toluene, alpha-pinene and hexane concentrations of 3.5 ± 0.6, 0.57 ± 0.02, 0.68 ± 0.11 and 0.66 ± 0.02 mg m^{-3}, respectively, circulated inside the fibers (air/air scenario). The clean air flow rate was set constant at 200 mL min^{-1} regardless of the EBRT tested. The inlet and outlet VOC concentrations in the simulated odorous stream and the outlet concentration in the clean air were periodically measured until the standard deviation of three consecutive measurements was lower than 10%, and the VOC mass balance over the reactor was evaluated to ensure the accuracy of the results obtained. The experiment was repeated by circulating MSM at 200 mL min^{-1} instead of clean air through the lumen of the HF-MBR (air/liquid scenario).

2.4 Operating procedure

Prior to process start-up, an abiotic test was conducted to assess any potential odorant removal due to adsorption or photolysis in the experimental set-up. The inlet and outlet VOC concentrations were periodically monitored for 5 days at an EBRT of 1 min in the absence of microbial activity (before inoculation and BF packing with compost).

The bioreactors were inoculated with 250 mL of activated sludge previously centrifuged at 10000 rpm for 10 min and resuspended in MSM at a concentration of 6.8 g L^{-1}. The influence of the EBRT on the odorant removal efficiency (RE) in the BF and BTF was evaluated at 48, 18 and 8 s. At day 78 (EBRT of 8 s), the packing material of the BF was removed and half of the compost was mixed with Kaldness K1 plastic rings (Evolution Aqua Ltd., UK) due to the high pressure drop (ΔP) recorded in this bioreactor. At day 95 the BF was stopped, while the EBRT of the BTF was further decreased to 4 s for 22 days. The removal performance of the HF-MBR was evaluated at similar EBRTs (43, 34 and 16 s) for 95 days. However, due to the unstable and low VOC abatement performance recorded in this system, the EBRT was increased to 84 s in the last operating period.

The gas concentration of the VOCs was daily measured at both inlet and outlet sampling ports of each bioreactor. Liquid samples of 20 mL were periodically withdrawn from the recycling liquid in the BTF and HF-MBR, replaced with MSM and filtered through a 0.22 μm filter in order to monitor the pH and the concentration of sulfate, dissolved total organic carbon (DOC), dissolved inorganic carbon (DIC) and dissolved total nitrogen (DTN). Distilled water was daily supplied to the systems to replace water losses by evaporation. Likewise, the ΔP in the three bioreactors and the temperature and moisture content in the inlet odorous emission were periodically recorded.

2.5 Analytical procedures

Gas samples for the analysis of the target odorants were collected in 250 mL glass bulbs (Sigma-Aldrich) and pre-concentrated for 10 min using 85 μm PDMS/Carboxen SPME

157 fibers (Supelco, Bellefonte, USA). The SPME fibers were injected in a GC-FID (Varian
158 3900) equipped with a SupelcoWax (15 m×0.25 mm×0.25 µm) capillary column. Oven,
159 injector and detector temperatures were maintained at 40, 300 and 300 ºC, respectively.
160 The flowrates of H_2 and air were fixed at 30 and 300 mL min^{-1}, N_2 being used as the
161 carrier gas at 1 mL min^{-1} and make-up gas at 25 mL min^{-1}. The pH of the recycling
162 media was measured using a pH/mV/°C meter (pH 510 Eutech Instruments, Nijkerk, the
163 Netherlands). Sulfate concentration was determined by HPLC-IC using an IC-Pak
164 Anion HC (150 mm × 4.6 mm). DOC, DIC and DTN were measured using a TOC-
165 VCSH analyzer (Shimadzu, Tokyo, Japan) coupled with a total nitrogen
166 chemiluminesce detection module (TNM-1, Shimadzu, Japan). The moisture content
167 and temperature in the influent odorous stream was recorded using a Testo 605-H1
168 thermohygrometer (Testo AG, Germany), and the ΔP in the bioreactors was determined
169 by means of a differential pressure meter using water as the manometric fluid.

170

171 **2.6 Microbiological procedures**

172 In order to evaluate the richness and composition of the bacterial communities present
173 in the bioreactors, biomass samples of the inocula (both fresh activated sludge (1) and
174 activated sludge after mixing with compost (2)) and biomass samples collected from the
175 bioreactors at the end of their operation (BF (3), BTF (4), HF-MBR recycling liquid (5)
176 and HF-MBR biofilm (6)) were collected and stored immediately at – 20ºC. The
177 genomic DNA was extracted according to Lebrero et al. (2012). The PCR mixture (50
178 µL) was composed of 25 µL of BIOMIX ready-to-use 2× reaction mix (Bioline,
179 Ecogen) containing reaction buffer, magnesium, deoxynucleotide triphosphates
180 (dNTPs), Taq polymerase and additives, 1 or 2 µL of the extracted DNA, PCR primers

968-F-GC and 1401-R (10µM) (Sigma- Aldrich, St. Louis,MO, USA) for bacterial 16S rRNA gene amplification, and Milli-Q water up to a final volume of 50 µL. The PCR thermo-cycling program used was previously described in Lebrero et al. (2012). The DGGE analysis of the amplicons was performed with a D-Code Universal Mutation Detection System (Bio Rad Laboratories) using 8% (w/v) polyacrylamide gel with a urea/formamide denaturing gradient from 45 to 65%. The DGGE running conditions were applied according to Roest et al. (2005). The gels were stained with GelRed Nucleic Acid Gel Stain (biotium) for 1 h and the obtained DGGE patterns processed using the GelCompar IITM software (Applied Maths BVBA, Sint-Martens-Latem, Belgium). After image normalization, bands were defined for each sample using the bands search algorithm within the program. Similarity indices of the compared profiles were calculated from the densitometric curves of the scanned DGGE profiles by using the Pearson product–moment correlation coefficient (Häne et al. 1993). The peak heights in the densitometric curves were also used to determine the Shannon–Wiener diversity index (H), which considered both the relative number of the DGGE bands (richness) and their relative intensities (evenness):

$$H = -\sum \left[P_i \ln(P_i) \right]$$

where P_i is the importance probability of the bands in a lane ($P_i = n_i/n$, where n_i is the height of an individual peak and n is the sum of all peak heights in the densitometric curves).

Sequencing and DNA sequence analysis

Selected bands were excised from the DGGE gel in order to identify the bacteria present in the samples above described. The procedure was previously described in Lebrero et

al. (2011). The taxonomic position of the sequenced DGGE bands was obtained using the RDP classifier tool (50% confidence level) (Wang et al. 2007). The closest matches to each band were obtained using the BLAST search tool at the NCBI (National Centre for Biotechnology Information) (McGinnis and Madden, 2004). Sequences were deposited in GenBank Data Library under accession numbers KF112977- KF112995.

3. Results

3.1 Packing material characterization

Polyurethane foam presented a notably lower density and wet bed density (0.01 and 0.30 g mL^{-1}, respectively) than compost (0.23 and 0.87 g mL^{-1}, respectively), but a ~25% higher porosity (96% vs. 72%). Conversely, its water retention capacity (0.12 L_{water} $L_{polyurethane}^{-1}$) was significantly lower than that of compost (0.68 L_{water} $L_{compost}^{-1}$). Finally, the pH of compost was slightly acidic (5.3) and lower than that recorded for polyurethane foam (6.3).

3.2 Abiotic VOC mass transfer characterization of the HF-MBR

When air circulated in both sides of the membrane, the four VOCs were equally transported regardless of their hydrophobicity and size, the transport efficiency increasing linearly with the gas residence time (Fig. 2A). Low mass transport efficiencies (5 - 8%) were observed at 7 s of EBRT, increasing to ~17% and 31% at 16 and 30 s, respectively, regardless of the odorant. At 45 s, the transport through the membrane increased to 48, 49, 54 and 54% for alpha-pinene, MeSH, toluene and hexane, respectively. Maximum mass transport efficiencies were observed for hexane at

60 s of EBRT (65%), while slightly lower values were recorded for toluene and MeSH (62%), and alpha-pinene (57%). Under the gas/liquid scenario, the mass transfer of the soluble VOCs noticeably increased compared to the air/air scenario, while the presence of the aqueous phase significantly hindered the transport of the more hydrophobic VOCs (Fig. 2B). Thus, MeSH was almost completely transferred to the liquid phase (>90%) at EBRTs higher than 16 s, its transport decreasing to 77% at an EBRT = 7 s. Toluene transfer efficiencies > 92% were also achieved at EBRTs > 45 s, with lower values recorded at 30 s (84%), 16 s (66%) and 7 s (43%). Similarly, 88% of alpha-pinene was transferred at an EBRT of 60 s, while at 7 s only 41% of this terpene passed through the membrane. Finally, the mass transfer efficiency of hexane decreased from 18% to 6% when decreasing the EBRT from 60 to 7 s, respectively.

3.3 Influence of the EBRT on the removal performance and pressure drop

Steady state MeSH (Fig. 3A), toluene (Fig. 3B) and alpha-pinene (Fig. 3C) removal efficiencies (REs) were rapidly achieved in the BF after inoculation (2-4 days), while 8 days were necessary for hexane RE stabilization (Fig. 3D). Following this rapid start-up, steady MeSH, toluene and alpha-pinene REs > 99% and hexane RE of 97.7 ± 0.8% were recorded at an EBRT of 43 s. During this first period, the ΔP remained always < 4 mmH_2O, increasing to ~50 mmH_2O by day 28 (Fig. 4A). The subsequent decrease in EBRT to 18 s (EBRT significantly lower than those typically used in biofiltration of 60-120 s) did not affect the VOC abatement performance. Hence, despite the BF was able to maintain MeSH, toluene and alpha-pinene REs of 98.4 ± 1.4%, 98.8 ± 0.9% and 98.9 ± 0.7%, respectively, and slightly lower hexane REs (96.1±1.9%), the decrease in EBRT resulted in an additional increase in ΔP to 186 ± 10 mmH_2O. A further reduction

252 in the EBRT to 8 s caused an initial deterioration in the removal capacity of the biofilter
253 (REs of 62, 60, 66 and 41% for MeSH, toluene, alpha-pinene and hexane, respectively,
254 by day 57) concomitant with an ΔP increase up to 502 ± 21 mmH_2O and a gradual
255 drying of the packing material. Therefore, the irrigation frequency was increased by day
256 58, which mediated a rapid restoration of the previous VOC removal performances
257 together with a dramatic increase in the ΔP to values > 2 mH_2O by day 77. In order to
258 decrease the ΔP, half of the compost of the BF packing material was replaced by plastic
259 rings by day 78. A subsequent deterioration of the toluene and hexane RE was observed
260 (minimum REs of 35.2 and 41.8%, respectively) followed by a performance
261 stabilization at steady toluene REs of 98.0 ± 0.7% and hexane REs of 93.7 ± 0.7% after
262 3 and 10 days, respectively. On the other hand, MeSH and alpha-pinene REs were not
263 affected by the packing replacement and steady values of 98.0 ± 1.5% and 98.8 ± 1.4%
264 were maintained at an EBRT = 8 s. The renewal of the packing material resulted in an
265 initial decrease in the ΔP to ~200 mmH_2O, although it rapidly increased again up to 1.3
266 mH_2O by day 94.

267

268 In the BTF, MeSH (Fig. 5A), toluene (Fig. 5B) and alpha-pinene (Fig. 5C) REs > 99%
269 were achieved after 12, 5 and 8 days of acclimation, respectively, while steady hexane
270 REs of 94.8 ± 1.7% were recorded 18 days after the start-up of the system (Fig. 5D).
271 This significantly higher acclimation times compared to the BF were due to the lack of
272 an inherent microbial diversity as that present in the compost. The ΔP during this period
273 did not exceed 5 mmH_2O (Fig. 4B). Likewise, MeSH, toluene and alpha-pinene REs >
274 99% and hexane RE of 91.8 ± 3.9% were maintained at an EBRT of 18 s. The ΔP
275 values also increased up to 10 mmH_2O by day 51. At an EBRT of 8 s, MeSH and
276 toluene were almost completely removed, while alpha-pinene RE slightly decreased to

98.6 ± 1.8%. A period of instability in the hexane removal performance was observed until day 79, followed by a performance stabilization at RE = 96.1 ± 2.2%. During this period, the ΔP fluctuated between 6 and 23 mmH_2O. By day 95 the EBRT was further deceased to 4 s, and steady REs of 97.4 ± 2.5%, 98.9 ± 0.7 and 98.1 ± 1.5% for MeSH, toluene and alpha-pinene were immediately achieved. On the other hand, hexane removal decreased to 88.4 ± 1.1% and steady ΔP of 29 ± 4 mmH_2O were recorded at the lowest EBRT.

After 10 days of operation, MeSH REs > 93% were recorded in the HF-MBR at 43, 34 and 16 s of EBRT (Fig. 6A). When the EBRT was increased to 84 s by day 95, MeSH RE remained constant for 4 days, steadily decreasing afterwards to a minimum value of 68.5% by day 101. Membrane cleaning at day 102 allowed for the recovery of MeSH removal, which finally stabilized at 98.4 ± 1.7%. Toluene RE fluctuated between 66.8% and 99.0% when the HF-MBR was operated at an EBRT of 43 s (Fig. 6B). When the EBRT was decreased to 34 and 16 s, toluene removal stabilized at ~96.0%. By day 95, at an EBRT of 84 s, toluene RE suddenly decreased to minimum values of 72.4%, increasing to 97.6 ± 2.4% after membrane cleaning. A stable alpha-pinene abatement was not achieved regardless of the EBRT (Fig. 6C). Initially, alpha-pinene RE increased gradually up to 96.7%, but decreased subsequently to RE of 69.7% by day 20. After membrane cleaning at day 21, the alpha-pinene removal progressively increased to 94.8% at an EBRT of 34 s. Three additional membrane cleanings were performed due to periodic deteriorations in the MBR abatement performance by day 39 (EBRT = 34 s, alpha-pinene RE increased to 92% afterwards), by day 72 (EBRT = 16 s, followed by a maximum RE of 99%) and by day 102 (EBRT = 84 s, alpha-pinene RE subsequently increased to values ranging from 80 to 99%). Finally, low hexane REs were recorded

during the entire experimentation period (Fig. 6D). At an EBRT of 43 s, average hexane REs of 23.0 ± 2.5% were observed until day 44, followed by a decrease in the RE to 10.0% and a subsequent gradual increase up to 58.4% by day 63. The RE decreased afterwards and remained constant at 38.3 ± 6.2% regardless of the membrane cleaning or the EBRT. The final increase in EBRT to 84 s did not change significantly the hexane removal performance, with steady values of 44.9 ± 2.5% recorded by the end of the experimentation period. Pressure drop values ranged between 42 and 159 mmH_2O at EBRTs of 43 and 34 s, decreasing to 9 mmH_2O after the second membrane cleaning by day 39 (Fig. 4C). However, the ΔP increased again by day 64 to 82 ± 13 mmH_2O. Surprisingly, the membrane cleaning by day 72 resulted in an initial increase in the ΔP to 180 mmH_2O, steadily decreasing afterwards to 51 ± 9 mmH_2O. The highest ΔP was recorded at an EBRT of 84 s (192 mmH_2O), gradually recovering previous values after membrane cleaning by day 102.

Liquid samples from the BF were only withdrawn during the first 30 days of experimentation due to the lack of leachate from that day on. DOC and DTN values ranging from 91 to 370 mg L^{-1} and from 460 to 770 mg L^{-1}, respectively, and sulphate concentration of 1569 ± 28 mg L^{-1} were recorded during that period. Sulphate production clearly confirmed the mineralization of MeSH, since a sulphate-free MSM was employed. In the BTF recycling liquid, the DOC remained stable at 47.2 ± 7.2 mg L^{-1}, while the DTN initially increased from 170 up to 287 mg L^{-1} by day 21 probably due to water evaporation, stabilizing afterwards at ~269 ± 14 mg L^{-1} until day 54 and decreasing again to stable values of 144 ± 19 mg L^{-1}. Sulphate concentration in this recycling media increased from 245 to 3532 mg L^{-1} by day 117. Finally, the DOC steadily decreased from initial values of 35 to ~5 mg L^{-1} by day 103 in the HF-MBR,

whereas the DTN remained stable at 171 ± 29 mg L^{-1}. The sulphate concentration was always <5 mg L^{-1}, sporadically increasing up to 340 mg L^{-1}. In this particular bioreactor, it is not possible to ascertain sulphate accumulation in the recycling liquid due to the frequent membrane cleaning, which were accompanied by a significant media replacement.

3.4 Bacterial population dynamics

The Shannon-Wiener diversity index takes into account both the number (richness) and the evenness of the species, typical values ranging from 1.5 to 3.5 (low and high species evenness and richness, respectively) (McDonald 2003). All samples exhibited high diversity indices (3.2 - 3.5) except for sample 3 (end of BF operation), which presented a slightly lower diversity index of 2.8 (Fig. 7). The analysis of the Pearson similarity coefficients showed a high similarity between the activated sludge inoculum and both the microbial community present in the BTF at the end of the experiment (samples 1 and 4 = 69.1%) and the recycling liquid of the HF-MBR (samples 1 and 5 = 70.5%). In addition, the bacterial community initially present in the activated sludge mixed with the compost exhibited a 72% similarity with the final communities present in the BF (samples 2 and 3 = 72%). The final composition of the microbial community established in the BF noticeably differed from the community in the BTF (48.9%) or in the HF-MBR (44.2%). Finally, the samples retrieved from the recycling liquid and the biofilm in the HF-MBR exhibited a high similarity (79.9%).

From the DGGE gel, 19 bands were sequenced (Fig. 7) and 6 different phyla were retrieved in the RDP database: *Proteobacteria* (8 bands), *Actinobacteria* (3 bands), *Nitrospira* (2 bands), *Verrucomicrobia* (2 bands), *Acidobacteria* (1 band) and

Chlamydiae (1 band), while two bands remained unclassified. The closest matches for every band (BLASTN) according to the NCBI database, together with its similarity percentages and sources of origin, are shown in Table 1.

4. Discussion

High REs were recorded in the BF for all the VOCs evaluated, including hexane (the most hydrophobic VOC), even at an EBRT of 8 s. However, the operation at low EBRTs and the progressive deterioration of the packing material (loss of compost structure and compaction) resulted in high pressure drops across the packed bed ($\Delta P >$ 14800 Pa m_{bed}^{-1}). In this context, the maximum compression energy requirements (W) at each EBRT can be estimated based on the corresponding gas volumetric flow rate (F, $m^3\ s^{-1}$) and the ΔP measured across the packing media (Pa m_{bed}^{-1}), for a standard blower efficiency of 0.7, according to:

$$P = \frac{F \times \Delta P}{0.7}$$

The analysis of the compression energy requirements and its comparison with the recommended maximum cost-effective compression energy needs (calculated from a maximum cost-effective value of ΔP of 1500 Pa m_{bed}^{-1}, Estrada et al. 2012) clearly showed that the operation of the compost-BF at EBRTs lower than 19 s might compromise the economic viability of odour abatement (Fig. 4D). Indeed, the development of high ΔP in compost-based BFs within a short operation period has been frequently reported in the literature: Dorado et al. (2012) observed ΔP of 2000 Pa m_{bed}^{-1} in a BF packed with compost-covered clay pellets, while Estrada et al. (2013) recorded ΔP over 4000 Pa m_{bed}^{-1} after 32 days of operation of a compost-based biofilter. Thus, in spite of the advantages of this packing material (a high diversity of indigenous

375 microbial species, high nutrient content, good water retention and porosity, low cost and
376 availability), its poor structural stability often entails a reduced bed lifespan.
377 Consequently, a stable and efficient removal of a wide hydrophobicity range of odorants
378 can be achieved in biofilters when properly operated, while energy requirements often
379 result in process operation at high EBRTs with a frequent media replacement.

380

381 In terms of process economics and land requirements, BTFs overcome BFs due to their
382 high VOC removal performance and low ΔP at EBRTs as low as 4 s. In this context,
383 high REs have been reported in literature for H_2S, MeSH and toluene in laboratory and
384 field scale BTFs at a wide range of EBRTs (ranging from 5 to 60 s) (Patria et al. 2001,
385 Ramirez et al. 2009, Yang et al. 2011). In our particular study, the continuous recycling
386 of the aqueous nutrient solution entailed slightly lower REs for the most hydrophobic
387 VOCs at the low gas residence times tested as a result of mass transfer limitations
388 (~88% hexane removal). Moreover, even at the low EBRTs applied in BTFs, the high
389 flow rates of odorous emissions to be treated still result in large bioreactor volumes: for
390 instance, the treatment of 50000-100000 m^3 h^{-1} would require a BTF volume of 50-110
391 m^3 at an EBRT of 4 s.

392

393 In this regard, membrane bioreactors are compact systems capable of providing higher
394 specific surface areas in lower reactor volumes, which constitutes the main advantage of
395 this configuration. Previous studies demonstrated the feasibility of applying membrane
396 bioreactors for treating individual industrial VOCs from waste gas emissions, although
397 biomass accumulation and clogging is still an important drawback to be solved
398 (Attaway et al. 2001, Álvarez-Hornos et al. 2011). Traditionally, biomass plugging was

399 only attributed to microporous or composite membranes due to the blockage of the
400 membrane pores by the biofilm (Attaway et al. 2002). However, an excessive biomass
401 growth also deteriorated the VOC abatement performance of the dense silicone
402 membrane tested in our experimental set-up. It was hypothesized that the accumulation
403 of biomass in the MBR lumen increased the pressure of the recycling liquid, which
404 compressed the thin silicone tubes, decreasing the cross sectional area and subsequently
405 reducing the actual gas residence time and increasing the ΔP of the odorous emission. In
406 addition, the formation of a thick biofilm on the membrane created an additional mass
407 transfer resistance, which likely resulted in a deterioration of the membrane
408 performance. This phenomenon was more evident for the less water soluble VOCs such
409 as alpha-pinene, whose RE significantly decreased due to membrane clogging. On the
410 other hand, dense PDMS membranes are reported to offer higher and constant REs,
411 together with a high permeability for the hydrophobic compounds (Kumar et al. 2008).
412 In our particular case, the abiotic study did not show any difference between the mass
413 transport efficiency of the 4 target VOCs in the air/air scenario, while hexane mass
414 transport efficiency was the lowest in the air/liquid scenario. In this context, some
415 authors have reported how the sorption and diffusivity across the membrane of one
416 component can be modified due to the interactions with other components (Kraakman et
417 al. 2007). Nevertheless, and in spite of the low transport efficiencies observed under the
418 air/liquid scenario, the formation of a biofilm increased the concentration gradients of
419 the pollutants through the membrane as observed during biotic operation. For instance,
420 while only 11% of hexane was transported through the membrane under the air/liquid
421 scenario, an average RE of 38.3% was recorded under biotic operation. Similarly, both
422 MeSH and toluene exhibited an improved biotic mass transport regardless of the EBRT
423 tested. The MBR configuration could have also played an important role in the results

here obtained, since although HF-MBRs offer higher specific gas-liquid surface areas (~2700 m^2 m^{-3}), flat sheet configurations are easier to operate in terms of membrane cleaning and replacement (Ergas and McGrath 1997). Thus, although membrane bioreactors constitute a promising alternative for treating gaseous emissions containing soluble and moderately soluble VOCs such as MeSH, toluene or alpha-pinene when clogging problems are overcome, the potential performance enhancement for the removal of hydrophobic compounds was not observed.

A highly diverse bacterial community was present in the three bioreactors, even under the low VOC mass loadings applied, an empirical finding also observed in bioreactors treating low odorant concentrations (Friedich et al., 2002, Lebrero et al., 2011). The maintenance of a high microbial diversity in the process is a key issue to ensure an efficient and stable long term bioreactor operation. The lowest bacterial diversity (H=2.8) was recorded in the BF after 95 days of operation, in spite of the higher diversity of the BF inoculum (mixture of activated sludge and compost). This decrease in diversity could be attributed to the proliferation of fungi and the subsequent increase in the fungal/bacteria ratio, whilst the presence of fungi was not analyzed in this study. The increase in the fungal biomass during the operation of organic-packed BFs has been previously reported by Prenafeta-Boldú et al. (2012) in a BF treating toluene.

Microorganisms potentially capable of degrading MeSH and VOCs were detected in this work. Species from the phylum *Proteobacteria* were retrieved in all samples: *Xanthomondaceae*-like bacteria (fragments 2 and 3) and *Rhodanobacter*-like bacteria have been previously detected in BFs, BTFs and membrane bioreactors treating odorous exhaust air, the latter being able to degrade aromatic hydrocarbons (Kristiansen et al., 2011, Lebrero et al., 2013). Fragment 6 was affiliated to the *Thiobacillus* genus, with a 99% of similarity to *Thiobacillus denitrificans* according to the BLAST analysis

(McGinnis and Madden 2004). This facultative anaerobic chemolithotroph is able to couple the oxidation of inorganic sulfur compounds to the reduction of oxidized nitrogen compounds (Beller et al. 2006). Different *Thiobacillus* bacteria were previously found in BFs and BTFs treating MeSH and other sulphur odorants (Maestre et al. 2010, Ramirez et al. 2009). Besides, *Alcaligenaceae* bacteria (fragment 7), detected with a high intensity in the BTF and the HF-MBR biofilm, have shown a high catabolic potential for aromatic compounds (Pérez Pantoja et al. 2011). *Actinobacteria*, which include aromatic and aliphatic degrading microorganisms, were also found in this study (fragments 9, 10, 11), mostly in the inoculum samples. Bacteria from the Genus *Gordonia* (fragment 9) within the Actinobacteria class, which have been previously retrieved from a bioreactor co-treating H_2S and toluene, were also detected in the BF and the HF-MBR samples with a high intensity (Gao et al. 2011). Several species within the genus *Gordonia* exhibit the capacity to degrade aliphatic and aromatic hydrocarbons while playing an important role in wastewater treatment bioreactors and biofilters (Arenskötter et al. 2004). *Nitrospira* related organisms are among the most diverse and widespread nitrifiers in natural ecosystems and biological wastewater treatment. Microorganisms within the *Nitrospira* phylum, which are able to degrade aromatic and non-aromatic hydrocarbons (Kristiansen et al., 2011, Lebrero et al., 2011), were observed in all samples except in the BF (fragments 12 and 13). On the other hand, microorganisms classified into the *Acidobacteria* phylum (fragment 16) were found in the samples from the BTF and the HF-MBR. These bacteria have been also retrieved from a BTF and a membrane bioreactor treating VOCs at trace level concentrations (Lebrero et al., 2012, Lebrero et al., 2013). Fragments 18 and 19 were unclassified bacteria predominantly found in the BTF (fragment 18) and the HF-MBR (fragment 19). Finally, it is also worth noting the high similarity (~80%) observed between the

474 microbial population in the biofilm of the HF-MBR and in the recycling suspended
475 culture.

476

477 Conclusions

478 To the best of our knowledge, this work constitutes the first comparative study of a HF-
479 MBR and two conventional biotechnologies (BF and BTF) in terms of odorant
480 abatement capacity and energy requirements. The BTF was the most cost-effective
481 technology, offering a high VOC abatement at low EBRTs and pressure drops.
482 Conversely, the operation of the BF at low EBRTs entailed high pressure drops across
483 the bed, which in turn results in prohibitive operating costs. The HF-MBR provided a
484 good abatement performance for the soluble odorants, although unstable alpha-pinene
485 and low hexane removals were recorded in this bioreactor configuration, this low
486 performance being associated to membrane clogging due to biomass overgrowth.
487 Hence, the successful implementation of MBR for odour treatment still requires further
488 research on biofilm accumulation control to avoid operational problems such as
489 hindered pollutant diffusion or reactor clogging.

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590

Figure captions

Figure 1. Schematic representation of the experimental set-up.

Figure 2. Influence of the EBRT on the transport efficiency of MeSH (×), toluene (○), alpha-pinene (□) and hexane (♦) through the membrane in the air/air (A) and air/liquid (B) scenarios.

Figure 3. Time course of the inlet (○) and outlet (+) concentrations, and removal efficiency (▲) in the biofilter for MeSH (A), toluene (B), alpha-pinene (C) and hexane (D). Vertical dashed lines represent the changes in EBRT, the vertical continuous line the change in the biofilter irrigation rate and the vertical dotted line the change of the biofilter packing material.

Figure 4. Time course of the pressure drop in the biofilter (A), the biotrickling filter (B) and the membrane bioreactor (C). Dashed vertical lines represent the changes in EBRT, the continuous vertical line the change in the biofilter irrigation rate and the vertical dotted arrows the membrane cleanings.

Figure 5. Time course of the inlet (○) and outlet (+) concentrations, and removal efficiency (▲) in the biotrickling filter for MeSH (A), toluene (B), alpha-pinene (C) and hexane (D). Vertical dashed lines represent the changes in EBRT.

Figure 6. Time course of the inlet (○) and outlet (+) concentrations, and removal efficiency (▲) in the hollow-fiber membrane bioreactor for MeSH (A), toluene (B), alpha-pinene (C) and hexane (D). Vertical dashed lines represent the changes in EBRT and the vertical continuous lines the membrane cleanings.

Figure 7. Bacterial DGGE profiles. Sample names and Shannon diversity indices are indicated in the upper part of the gel: (1) fresh activated sludge, (2) activated sludge after mixing with compost, (3) BF, (4) BTF, (5) HF-MBR recycling liquid, and (6) HF-

615 MBR biofilm. The sequenced DGGE bands are indicated with an arrow (►) and the
616 corresponding number of each band.

Figure 1

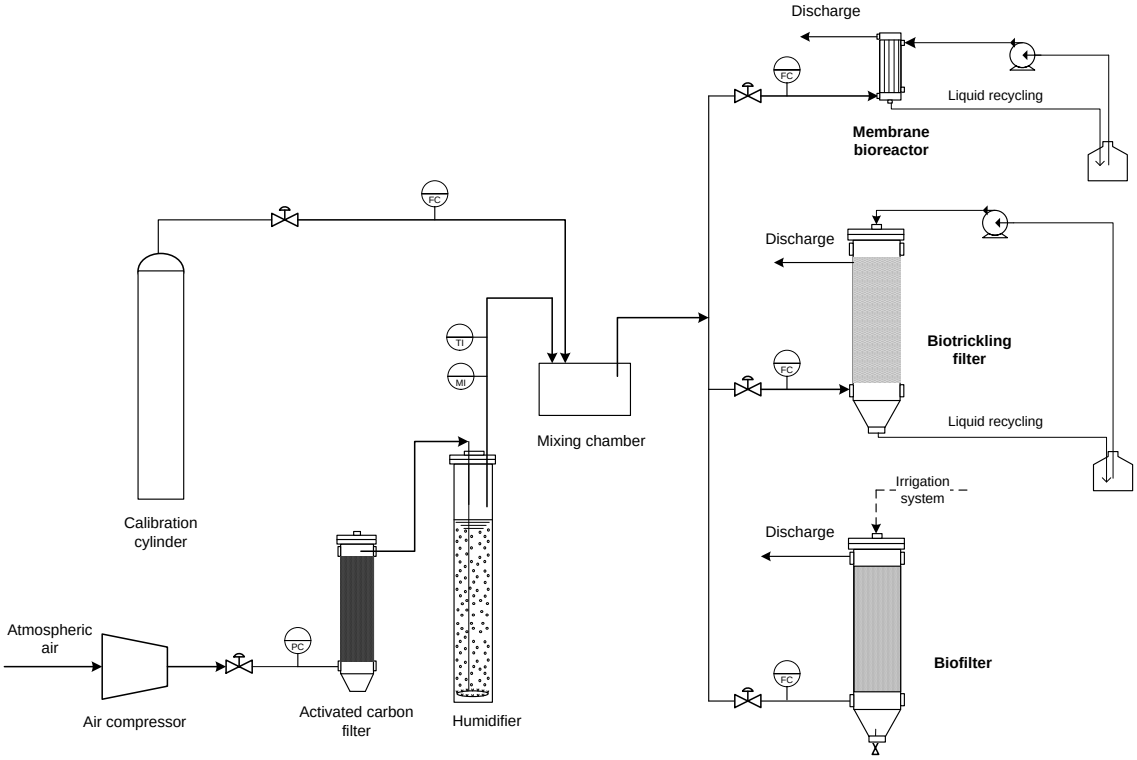

Discharge
FC
Liquid recycling
Membrane bioreactor
FC
Discharge
Biotrickling filter
TI
MI
FC
Liquid recycling
Mixing chamber
Irrigation system
Discharge
Calibration cylinder
Biofilter
FC
Atmospheric air
PC
Air compressor
Activated carbon filter
Humidifier

Figure 2

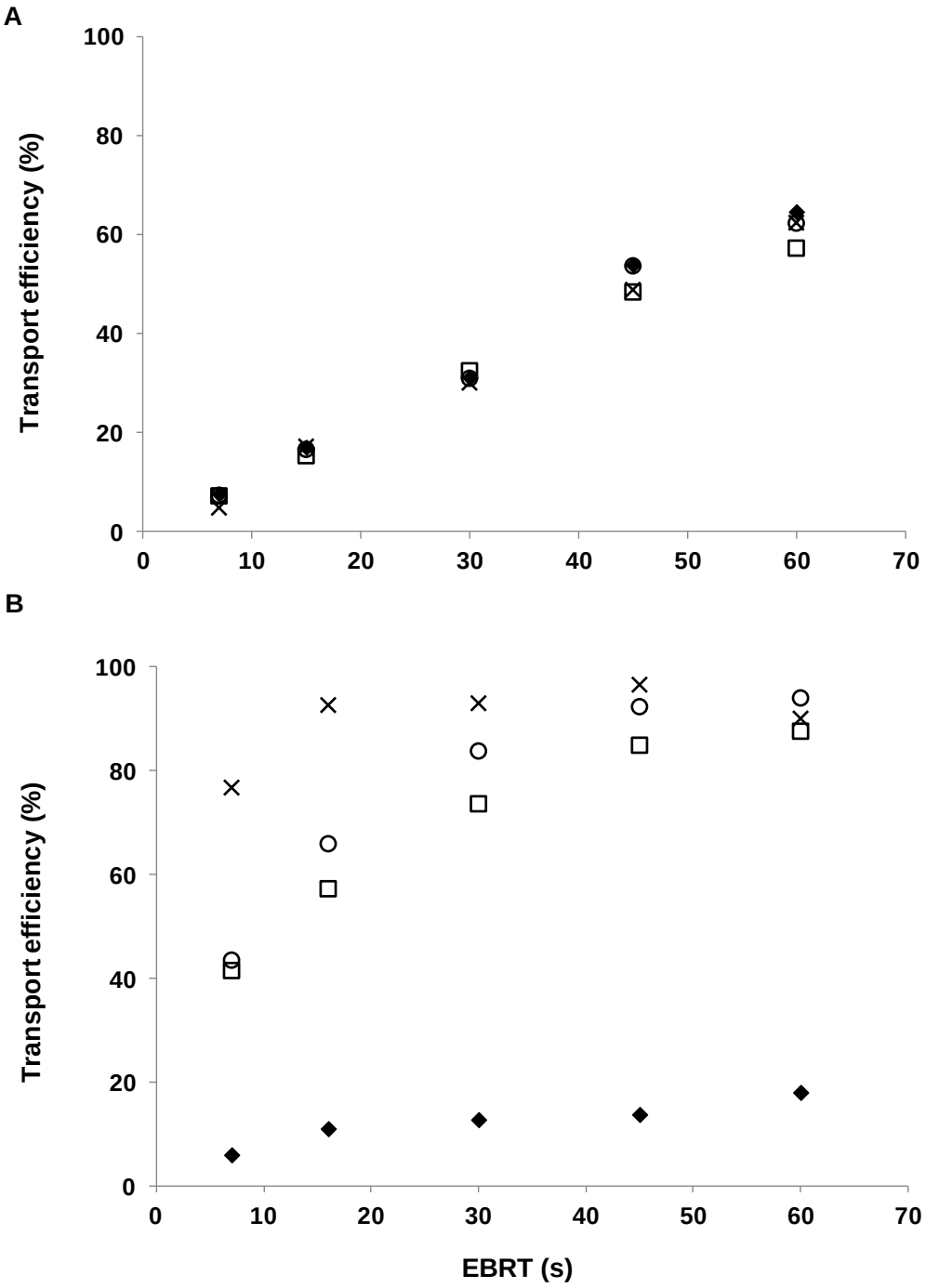

A
Transport efficiency (%)
0
20
40
60
80
100
0
10
20
30
40
50
60
70
B
Transport efficiency (%)
0
20
40
60
80
100
0
10
20
30
40
50
60
70
EBRT (s)

Figure 3

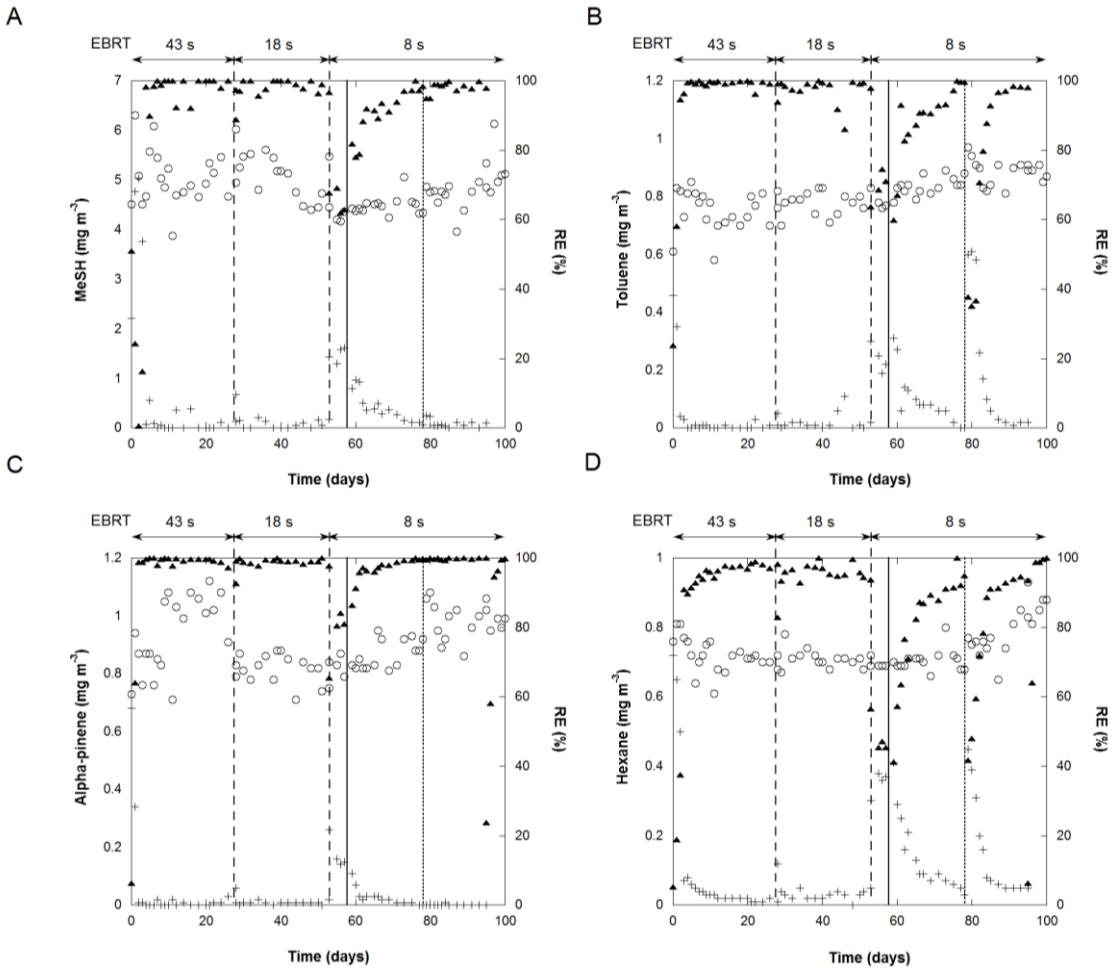

A
EBRT
43 s
18 s
8 s
MeSH (mg m-3)
RE (%)
Time (days)
B
Toluene (mg m-3)
C
Alpha-pinene (mg m-3)
D
Hexane (mg m-3)

Figure 4_ revised

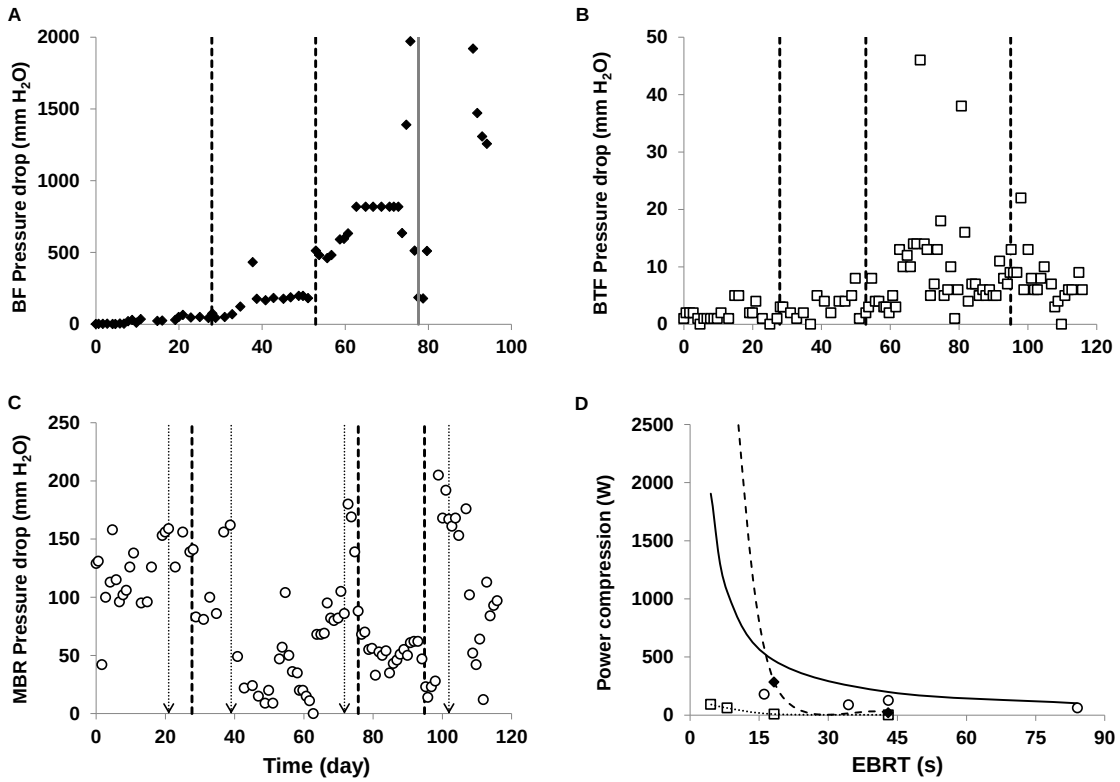


Figure 5

Figure 5

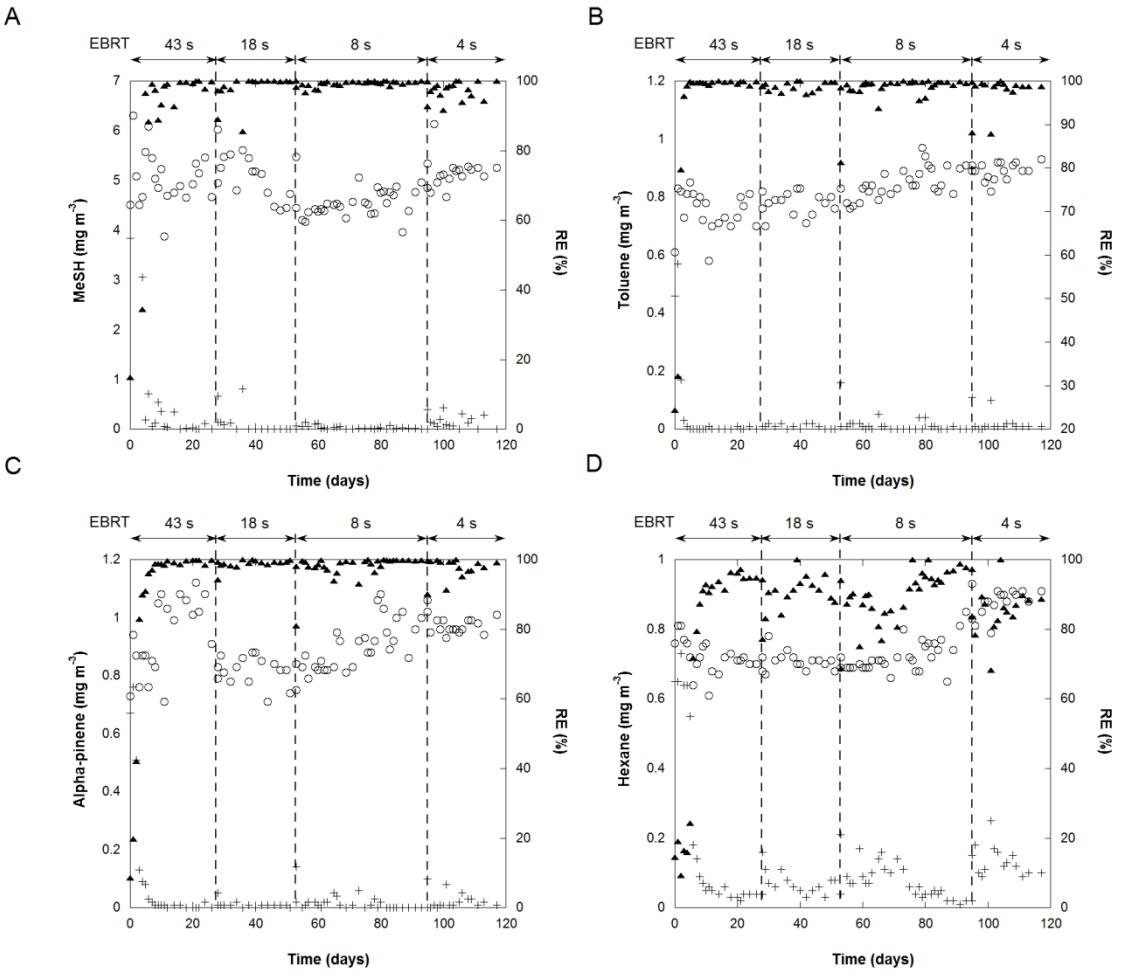


Figure 6

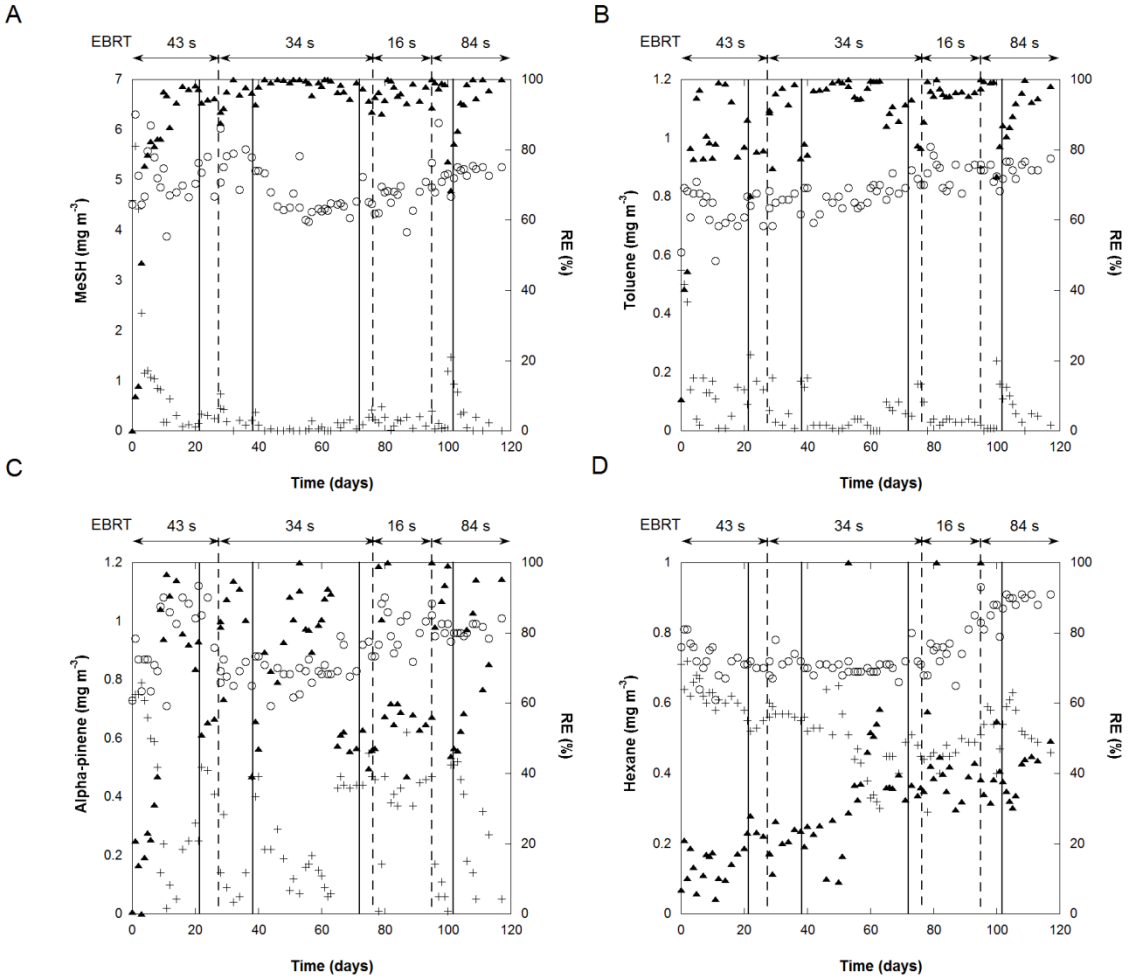
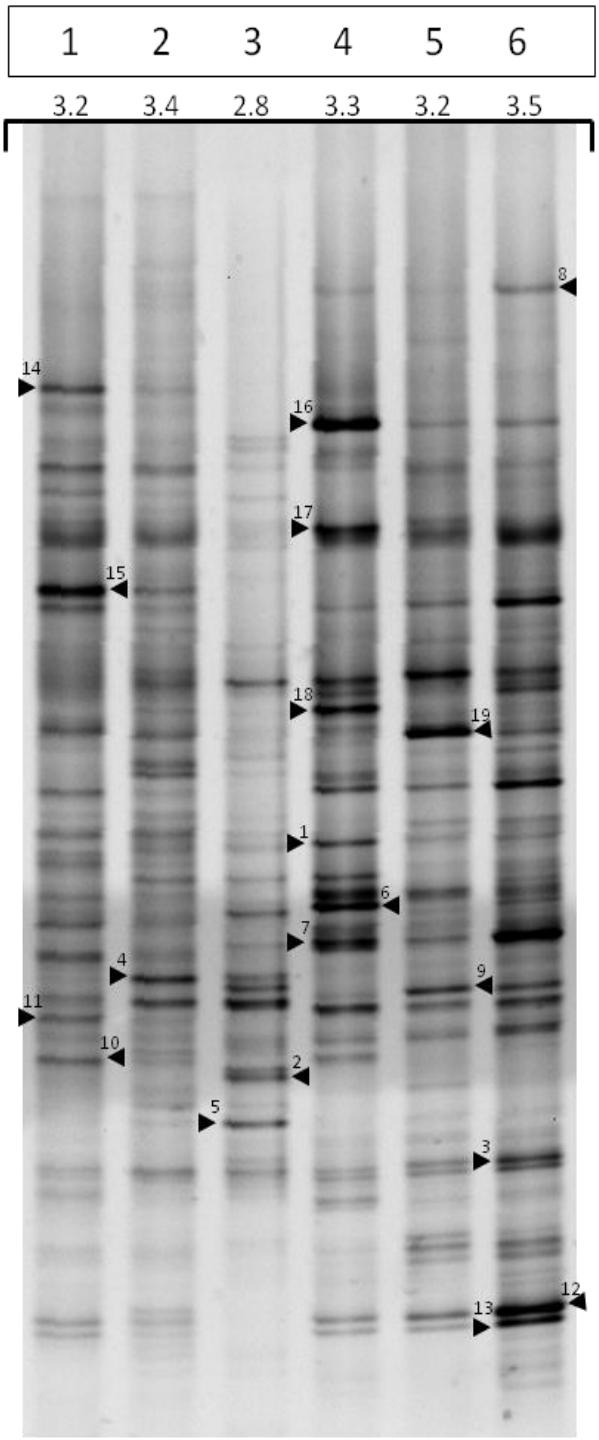

A
EBRT
43 s
34 s
16 s
84 s
MeSH (mg m-3)
RE (%)
Time (days)
B
Toluene (mg m-3)
C
Alpha-pinene (mg m-3)
D
Hexane (mg m-3)

Figure 7



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