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**Environmental Progress
& Sustainable Energy**

**Characterization and evaluation of poplar and pine wood in
twin biotrickling filters treating a mixture of NH₃, H₂S,
butyric acid and ethylmercaptan**

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Editor

Comments to the Author:

There are still issues with language and grammar. Please have the manuscript proofread.

Reviewing: 1

Comments to the Author

It is a good contribution using organic packing material for treatment of gas phase pollutant using biotrickling filters

Reviewing: 2

Comments to the Author

-

Characterization and evaluation of poplar and pine wood in twin biotrickling filters treating a mixture of NH₃, H₂S, butyric acid and ethylmercaptan

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Abstract

Biotrickling filters for waste gas treatment are often packed with expensive, inert packing materials. In this work, poplar and pine wood chips were evaluated as low-cost packing materials in two biotrickling filters for the simultaneous treatment of a mixture of organic and inorganic volatile compounds. Bioreactors were operated at gas contact times of 22-34 s. Inlet loading rates of $3.5 \pm 1.0 \text{ gN-NH}_3 \text{ m}^{-3}\text{h}^{-1}$ and $6.5 \pm 1.1 \text{ gS-H}_2\text{S m}^{-3}\text{h}^{-1}$ were supplied, while ethylmercaptan (EM) and butyric acid were fed at loads of $3.6 \pm 1.2 \text{ g m}^{-3}\text{h}^{-1}$ and $6.0 \pm 2.1 \text{ g m}^{-3}\text{h}^{-1}$, respectively. A thorough characterization of both ~~support media~~ packing materials revealed some differences in the physical-chemical properties, mainly in their water retentivity and buffer capacity. Despite of ~~these~~ such differences, both bioreactors performed similarly. Bioreactors were able to achieve complete removal of NH₃ and butyric acid, while H₂S and EM removal efficiencies over 90% and 70%, respectively, were found. N-species analyses in the leachate proved high nitrification rates ~~for in~~ both woods biotrickling filters. ~~The~~ Control of pH ~~control~~ was essential for maintaining nitrification activity. Other oxidation processes were hardly affected by pH changes. Both woods showed potentially attractive as ~~support media~~ packing materials for biofiltration. Thus, availability and durability of woods are decisive factors to tip the balance.

Novelty or Significance. The work compares the performance of two biotrickling filters packed with two types of wood chips commonly used in biofilters. No previous works have directly compared the performance of two types of woods in biotrickling filters for the treatment of a range of organic and inorganic odorants because biotrickling filters are commonly packed with inert packing materials. Results indicated d that the two types of woods tested behaved similarly and, more interestingly, showed equivalent treatment capacities than

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that of inert packing materials in the removal of a range of typical pollutants in odorant waste gases. Research is of particular interest for improving biofiltration knowledge ~~of biofiltration~~. In addition, ~~since inorganic packing materials commonly used in biotrickling filters are much more expensive than organic packing materials~~, this research has large practical implications in the cost-benefit of full-scale biotrickling filtration systems because inorganic packing materials commonly used in biotrickling filters are much more expensive than organic packing materials.

Keywords: Biotrickling filters, Organic media; packing characterization; odorants treatment, twin bioreactors

1 INTRODUCTION

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The use of bioreactors for gaseous effluents treatment is a widely recognized biotechnology that has been successfully applied during the last decades in a wide range of industries for the abatement of a wide spectrum of pollutants. Among ~~the~~ different configurations, biotrickling filters have demonstrated their capabilities to remove odorant pollutants in processes such as the treatment of gaseous emissions from wastewater treatment plants (WWTPs) or composting processes. However, biotrickling filters use inorganic packing materials such as plastic or ceramic beds because of the presence of a continuously flowing water phase over the packed bed. Such conditions could potentially damage organic packing materials and cause reactor flooding [1]. Regarding organic materials, the use of different types of wood chips has been reported in conventional biofilters, a bioreactor configuration without a continuous water phase flowing over the packing material [2-4]. The main advantages of wood chips as packing material are their low purchasing price, their capacity to act as water reservoir due to a high water holding capacity; as well as their capacity to avoid packing material compaction ~~of the material~~ [1]. Specifically, ~~their~~ water retentivity and water holding capacity of wood chips, which are favorable in comparison to inorganic packing materials, could be beneficial during unexpected situations such as a liquid phase recirculation failure or during the treatment of extremely dry streams at high

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3 67 | temperatures, which could end up in ~~drying out~~ the packing material dry out. However,
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5 68 | an organic material can be more rapidly exhausted and biodegraded under high water
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7 69 | content conditions, which may hinder its use in biotrickling filters. The number of
8
9 70 | studies with biotrickling filters packed with wood chips is scarce in literature [5-6].
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11 71 | Chen et al. [7]; studied the performance of two wood chips-based biofilters to reduce
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13 72 | odor, H₂S and NH₃ from swine barn ventilation air distinguishing two kinds of woods:
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15 73 | western cedar and oak wood. However, to the authors' knowledge there is no study
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17 74 | indicating if a particular kind of wood is more effective ~~than others when used in~~
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19 75 | biotrickling filters ~~to the authors knowledge~~. However, little attention has been paid to
20
21 76 | the specific characteristics of different types of woods in relation to biotrickling filters
22
23 77 | performance in terms of removal efficiency (RE), ~~even less~~ attention has been paid in
24
25 78 | trying to find evidences of advantages/disadvantages of using pine or poplar wood chips
26
27 79 | as packing materials [8]. The use of poplar and pine wood chips ~~results is~~ highly
28
29 80 | interesting from an economical perspective due to their affordability and low price (45-
30
31 81 | 60 € m⁻³ and 40-50 € m⁻³, respectively). Thus, it is interesting to study wood chips
32
33 82 | performance as packing material in-depth, since it is an easy-to-get media, landfill
34
35 83 | disposable and a ~~proven~~ cost-effective material ~~as confirmed in previous studies~~ [9]. In
36
37 84 | this sense, the present work is the first work that to compared twin biotrickling filters
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39 85 | packed with two different ~~kinds of woods~~ by an exhaustive evaluation in terms of media
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41 86 | characterization and bioreactors performance for the treatment of a multi-component
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43 87 | gaseous stream.

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45 88 | Regarding pollutants usually treated ~~by in biofiltration biofilters~~, NH₃ and H₂S are
46
47 89 | common ~~inorganic~~-volatile inorganic compounds widely studied due to their presence in
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49 90 | a range of ~~proecesses sites~~ such as composting plants, livestock facilities, fish processing
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51 91 | industries or WWTPs among others. NH₃ concentrations up to 120 ppmv and H₂S

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3 92 | concentrations in the range of 10-60 ppmv are often found in ~~those such~~ industries [1].
4
5 93 | EM and butyric acid are volatile organic compounds mainly present at low
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7 94 | concentrations, which may only lead to a ~~malodorous bad odor~~ problem. Butyric acid
8
9 95 | has a sour, sweaty smell and belongs to hydrophilic volatile fatty acids group typically
10
11 96 | generated when organic matter is decomposed under anaerobic conditions [10]. In turn,
12
13 97 | volatile organic sulfur compounds such as ethylmercaptan (EM) and dimethyldisulfide
14
15 98 | (DMDS) have lately received intensive attention because of their very low odor
16
17 99 | threshold, high toxicity, and potential corrosive effect [11]. Specifically, EM is a
18
19 100 | moderately soluble in water and toxic organic compound with an odor threshold as low
20
21 101 | as $0.7 \mu\text{g L}^{-1}$ (0.28 ppm_v) [12]. It has been also classified as one of the most annoying
22
23 102 | compounds in odor emissions [13]. Overall, the complex mixture used herein comprises
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25 103 | some of the most typical and most annoying pollutants released in real emissions. It is
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27 104 | important to highlight that the oxygen content might not limit microbial biodegradation
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29 105 | at the pollutants load typically encountered in these facilities [1].
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34 106 | Based on the promising results obtained in a previous study [9], the present work
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36 107 | focused on the evaluation of several properties of poplar and pine wood susceptible to
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38 108 | affect the biofiltration ~~process~~ process. In addition, this work focused and on the to
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40 109 | comparisone of the behavior of both materials under identical conditions in a
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42 110 | biotrickling filter configuration, treating a mixture of H₂S, NH₃, EM and butyric acid
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44 111 | during a period of more than three months.
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113 2 MATERIALS AND METHODS

114 2.1 Experimental setup and operating conditions of the bioreactors

115 | The experimental setup consisted of two parallel PVC biotrickling filters ~~made in PVC~~
116 | with a height of 70 cm and an internal diameter of 8.6 cm. Reactors were packed with

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3 117 | poplar and pine wood chips, respectively, up to a height of 50 cm, resulting in a packed
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5 118 | bed volume of 2.9 L per biofilter. The polluted air was supplied in up-flow mode. Inlet
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7 119 | H₂S and NH₃ concentrations were provided from pure gas cylinders and mixed with
8
9 120 | fresh air using digital mass flow controllers (Bronkhorst, The Netherlands). EM was fed
10
11 121 | by means of a double-head peristaltic pump (Mod. 403 U/VM2, Watson Marlow,
12
13 122 | England) that pumped air into glass bubblers containing liquid EM ~~97%~~(97% purity,
14
15 123 | Sigma Aldrich, United States). Pure butyric acid was fed by means of a microburette
16
17 124 | Multiburette 2S (Crison Inst. S.A., Spain). The liquid level in both bioreactors was kept
18
19 125 | constant by means of two peristaltic pumps (Mod. 302 S, Watson Marlow, England)
20
21 126 | controlled by a home-made LabWindows™ ~~CVI~~ application. ~~More d~~Detailed
22
23 127 | characteristics of the biofiltration setup can be found elsewhere [6].
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28 128 | Inoculation at ambient temperature (18 - 23°C) was carried out during 48 hours in both
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30 129 | reactors ~~at ambient temperature (18—23°C)~~ by continuous recirculation ~~during 48 hours~~
31
32 130 | of an activated sludge mixture at an initial concentration of 1.5 g VSS L⁻¹ containing i)
33
34 131 | enriched ~~ammonium-ammonium~~-oxidizing bacteria (AOB) ~~taken-withdrawn~~ from a pilot
35
36 132 | plant where partial nitrification was ~~achieved-taking place~~ and ii) aerobic sludge from a
37
38 133 | urban WWTP (Manresa, Spain). Use of aerobic sludge from WWTPs for inoculation is
39
40 134 | widely accepted since a wide spectrum of microorganisms is encountered [14-15]. A
41
42 135 | more detailed description of packing materials characteristics as well as the inoculation
43
44 136 | procedure of the reactors is provided in the Supplementary Material section S1. Several
45
46 137 | samples were extracted along the experimental period in order to identify ~~sulfur-sulfur-~~
47
48 138 | oxidizing and nitrifying bacteria. However, the organic nature of ~~the~~ wood chips made
49
50 139 | difficult to obtain DNA from biofilm samples to produce reliable results. Thus, ~~it was~~
51
52 140 | ~~not possible to characterize~~ characterization of the microbial communities in the
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3 141 | biotrickling filters was not possible. Either way, ~~to carry out~~ an in-depth ~~–~~microbial
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5 142 | characterization of biotrickling filters was not the scope of this work.

6
7 143 | Inlet concentrations of 48.5 ± 9.4 ppm_v of NH₃, 40.2 ± 3.1 ppm_v of H₂S, 11.7 ± 3.8 ppm_v
8
9 144 | of EM and 13.3 ± 3.4 ppm_v of butyric acid were kept constant throughout the
10
11 145 | experimental period, corresponding to loads of 3.5 ± 1.0 g N-NH₃ m⁻³ h⁻¹ ~~of N-NH₃~~, 6.5
12
13 146 | ± 1.1 g S-H₂S m⁻³ h⁻¹ ~~of S-H₂S~~, 3.6 ± 1.2 g EM m⁻³ h⁻¹ ~~of EM~~ and 6.0 ± 2.1 g butyric
14
15 147 | acid m⁻³ h⁻¹ ~~of butyric acid~~, respectively. Those are typical concentrations susceptible to
16
17 148 | be found at industrial facilities such as composting, food processing or WWTPs among
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19 149 | others [1-2, 16]. During the experimental period, a constant gas flow rate of 310 L h⁻¹
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21 150 | was fed to each biofilter, corresponding to an initial empty bed residence time (EBRT)
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23 151 | of 34 s. However, ~~due to operational failures~~ this initial value was significantly reduced
24
25 152 | in the poplar wood reactor (PPWR) due to operational failures. Bioreactors were
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27 153 | operated at a room temperature of $22 \pm 2^\circ\text{C}$ and the recirculation flow rate was set at 130
28
29 154 | mL min⁻¹. The liquid phase was continuously renewed by the automated supply of tap
30
31 155 | water. Make-up water flow rate varied between 600 and 2520 mL day⁻¹, corresponding
32
33 156 | to a hydraulic residence time (HRT) between 1.00 and 0.24 day. Thus, the Gas/Liquid
34
35 157 | ratio defined as the inlet gas flow rate divided by ~~the renovation of of the~~ fresh liquid
36
37 158 | renewal varied from 12400/1 to 2953/1. The pH control was set ~~on from~~ day 28 onwards
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39 159 | by means of the permanent addition of NaOH (0.02 g L⁻¹) in the make-up water flow.
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161 | **2.2 Analytical methods**

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49 162 | H₂S concentration was measured using an electrochemical H₂S sensor (Sure-cell, Euro-
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51 163 | Gas Management Services LTD, England) with a detection limit of 1 ppm_v. NH₃
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53 164 | concentration was determined after bubbling the gas stream in acidified water and ~~later~~
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55 165 | ~~on~~ passed through an ammonium flow analyzer later on [17]; with a detection limit of 5
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3 166 mg N-NH₄⁺ L⁻¹. ~~For EM and butyric acid determination, a A~~ calibrated Gas
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5 167 Chromatograph (6890N, Agilent Tech. S.A., Spain) was ~~employed~~used for EM and
6
7 168 butyric acid determination; with a detection limit of 2 ppm_v for both compounds.
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10 169 Chloride, N-ammonium, N-nitrite, N-nitrate, S-sulfate and P-phosphate ions
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12 170 concentration in leachate samples were determined in an ICS-1000 Ion Chromatograph
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14 171 (Dionex Corp., United States) equipped with an IonPac AS9-HC column with a
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16 172 detection limit of 5 mg L⁻¹ for all species. Leachate pH and conductivity were measured
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18 173 by means of a pH 28 sensor and a MicroCM 2100 sensor (Crison Instr. S.A., Spain),
19
20 174 respectively. According to the specifications of the instrumentation employed in this
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22 175 work, the following standard deviations were considered: 10% for EM and butyric acid
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24 176 RE, 1.5% for H₂S RE, 1-2% for species measured by ionic chromatography and 1% for
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26 177 the continuous flow analyzer. Regarding packing materials characterization, methods
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28 178 employed to evaluate materials properties are described elsewhere [18]. Finally, sulfur
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30 179 oxidation ~~processin~~-of bioreactors was verified through S-SO₄²⁻ production rates, which
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32 180 were calculated through mass balances as detailed in the Supplementary Material section
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36 181 S2.
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183 3 RESULTS

184 Packing materials characterization

185 The suitability of poplar and pine wood as packing material for biofiltration was
186 evaluated by means of different physical-chemical parameters commonly studied in
187 biofiltration (Tables 1 and 2). Among the natural carriers used in biofiltration, woods
188 are the most extensively used together with compost, peat and soil [19]. However, the
189 comparison of the behavior of different woods in biotrickling filters is still unexplored.
190 Elementary analyses were performed to identify the capacity of each packing material to

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3 191 potentially provide macronutrients such as nitrogen and phosphorous necessary for
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5 192 biomass growth. Both materials presented a similar nutrient content: 46-49% C, 0.3% N,
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7 193 less than 0.1% S and 0.05% P. Concerning the specific surface area, which was
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10 194 measured by the BET technique (Table 1), ~~wood-wood~~-based materials showed a
11
12 195 slightly lower specific surface area value (~~inferior to below~~ 1.3 m² g⁻¹) ~~than materials~~
13
14 196 ~~like compared to~~ compost and coconut fiber ~~but~~. A much lower specific surface area
15
16 197 was found compared to porous materials ~~like such as~~ carbons (up to 950 m² g⁻¹).
17
18 198 ~~The Packing materials~~ pH of packing materials was ~~close to neutral or~~ slightly acid (pH
19
20 199 ≈ 6.7 for pine wood chips) while the ir buffer capacity was between 35 and 50 mL SO₄²⁻
21
22 200 L⁻¹ (Table 1). Sorption capacities were determined for both dry and wet materials to
23
24 201 obtain information ~~regarding about~~ the interactions nature between the contaminant, the
25
26 202 packing materials and the aqueous phase. Poplar wood adsorption capacities of 0.05 and
27
28 203 0.06 mg toluene g⁻¹ packing material were achieved under dry and wet conditions,
29
30 204 respectively, according to the procedure detailed in Dorado et al. [17]. Pine wood
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32 205 showed a 30% decrease in its adsorption capacity (from 0.06 to 0.04 mg toluene g⁻¹
33
34 206 packing material) under wet conditions, which ~~can be considered are the common~~
35
36 207 normal operating conditions in biofilters. Larger reductions ~~of in~~ the adsorption capacity
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38 208 under wet conditions have been reported in other ~~common media~~ packing materials [20].
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40 209 In the materials presented herein, a lower water holding capacity and a similar porosity
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42 210 of both materials (0.88) could explain a minor reduction of such adsorption capacity.
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44 211 Moreover, the water retentivity measured, expressed as the water percentage lost per
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46 212 hour, revealed that both materials ~~can retain their water content~~ efficiently. In any case,
47
48 213 the maximum sorption capacity of the materials was less than 0.10 mg toluene g⁻¹
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50 214 material. The water holding capacity and water retentivity are related to packing
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52 215 materials ~~structural configuration. Depending on the material specific~~ structure, water
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3 216 | ~~Despite the fact that water~~ molecules can be more or less time retained in the material,
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5 217 | ~~but after a certain period of time without the supply of extra water,~~ all ~~media-packing~~
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7 218 | ~~materials might~~ lose most of ~~its-their~~ water content ~~after a certain period of time without~~
8
9 219 | ~~the supply of extra water~~. For instance, when dealing with a dry moisture stream, it
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11 220 | would be interesting to operate with materials with a large water retentivity ~~in-order-to~~
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13 221 | avoid packing material desiccation and allow microorganisms maintaining their activity.

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15 222 | In the case of wood chips as unique packing material, several studies employing
16
17 223 | conventional biofilters achieved the highest reduction efficiencies for odor
18
19 224 | concentration and NH₃ removal when keeping the filter media moisture content over
20
21 225 | 60% (wet basis) [7,21]. Thus, both parameters, ~~among others,~~ were considered key
22
23 226 | factors to take into account when choosing the most suitable packing material for a
24
25 227 | specific scenario.

26
27 228 | Regarding pressure drop ~~through the packed bed~~ (ΔP), intrinsic ΔP for dry packing
28
29 229 | materials was below 1 cm water column per meter of packing material height in both
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31 230 | cases (Table 2). Results agreed with typical ΔP ranges for ~~pressure-drop-through~~
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33 231 | packing materials [20]. Interestingly, ΔP slightly increased with the presence of water
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35 232 | inside the packing material even if this influence was more remarkable at higher
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37 233 | superficial velocities (data not shown). In the case of poplar wood, the ΔP ~~achieved~~ was
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39 234 | twice that obtained for pine wood, which ~~is-a-sign-of~~ ~~indicated~~ a higher resistance to air
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41 235 | flow due to the superficial rugosity of the material. Both materials were evaluated ~~at~~
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43 236 | ~~under~~ the same water content. ΔP ~~increases-increased~~ between 5 and 30% ~~over~~
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45 237 | ~~compared with that under~~ dry conditions, ~~which~~ did not have a significant impact in
46
47 238 | terms of energy consumption costs as shown in Table 2. Besides punctual episodes, ΔP
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49 239 | in both reactors never exceeded 7 cm of water column per meter of packing material
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51 240 | height (figure S1 in Supplementary Material) during the entire operational period. The
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3 241 electricity consumption was calculated ~~considering a kilowatt-hour cost of 0.08 € kWh⁻¹~~
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5 242 ~~and~~ by means of a previously reported empirical expression $P(\text{kW}) = 3.64 \cdot 10^{-4} \cdot Q$
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7 243 $(\text{m}^3 \text{ h}^{-1})$ [22] ~~considering a kilowatt-hour cost of 0.08 € kWh⁻¹~~. The increase in the
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9
10 244 electrical consumption due to the ΔP was estimated according to a mechanical energy
11
12 245 balance: $P(\text{W}) = \Delta P (\text{N m}^{-2}) \cdot Q (\text{m}^3 \text{ s}^{-1})$ where P is the consumption power, ΔP is the
13
14 246 pressure drop and Q is the flowrate circulating through the packing material.
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16 247 Regarding energy costs associated to blow the air through the packing material, a
17
18 248 difference of 2.5% between materials was found (Table 1 and 2). Therefore, the main
19
20 249 difference between packing materials laid in their purchase cost ~~of the support materials~~
21
22 250 and ~~their~~ durability. The purchase cost, which is directly related with the availability of
23
24 251 each wood, had a significant impact in the overall costs; not only because of the large
25
26 252 volumes usually required for biofilter construction but also because of packing materials
27
28 253 replacement due to ~~their~~ limited durability ~~caused by a low mechanical and chemical~~
29
30 254 ~~resistance~~. Table 1 shows the purchase price of both packing materials according to
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32 255 prices of year 2014, Spanish market. The durability was estimated according to previous
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34 256 experiences of suppliers (Melcourt, UK).
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258 Sulfur compounds removal

43 259 Regarding H₂S removal, both bioreactors maintained analogous trends. Initial REs
44
45 260 around 50% were measured, which increased gradually up to REs above 85% on day 13
46
47 261 and remained that high the rest of the study (Figure 1a and b). Both reactors were able to
48
49 262 biodegrade H₂S to SO₄²⁻ from the beginning of the experimental period ~~on~~ (Figure 2).
50
51 263 Since unexpected situations are likely to occur during real operation, some
52
53 264 malfunctioning episodes were used to evaluate the resilience capacity of wood chip-
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55 265 based biotrickling filters. Thus, EM RE varied significantly during the fluidization of the
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3 266 packing material due to a flooding episode, denoting a low capacity to face such
4
5 267 unexpected failure.

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7 268 Both bioreactors startup took around 20 days until achieving REs above 85% (Figure 1c
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9
10 269 and d). Nevertheless, after reinoculation of both reactors on day 34 to reactivate the
11
12 270 nitrification process, EM REs were lower than ~~those~~ before reinoculation. Two weeks
13
14 271 before reinoculation, EM REs of $94 \pm 5\%$ and $88 \pm 8\%$ were measured for PPWR and
15
16 272 pine wood reactor (PNWR), respectively, ~~while a. After day 34 onwards~~, average REs
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18 273 decreased down to $75 \pm 13\%$ and $83 \pm 16\%$ for PPWR and PNWR, respectively. It is
19
20
21 274 likely that flooding episodes in PPWR on days 37 and 58 negatively affected the EM
22
23 275 elimination, leading to ~~these such~~ significant differences in EM REs in comparison with
24
25 276 PNWR.

26
27 277 Both the startup period and unexpected operational changes lead to a significant
28
29 278 dispersion of results. Despite of such variability, a similar trend was found in terms of
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31 279 EC of sulfur compounds (figure S2 in Supplementary Material). Both reactors
32
33 280 performed similarly showing that the maximum EC was not reached for H₂S removal.
34
35 281 However, from day 13 onwards, a pseudo-stationary period was achieved and RE values
36
37 282 of $96 \pm 4\%$ and $97\% \pm 2$ were measured for PPWR and PNWR, respectively,
38
39 283 corresponding to maximum EC values of 6.5 ± 0.9 and $5.6 \pm 0.6 \text{ g m}^{-3} \text{ h}^{-1}$. A plateau in
40
41 284 the EC vs LR profile (figure S2b and S2d) was found at around $2 \text{ g EM m}^{-3} \text{ h}^{-1}$,
42
43 285 particularly in the case of the PPWR reactor.

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45
46 286 Moreover, oxidation of reduced sulfur compounds was verified by assessing the S-SO₄²⁻
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48 287 production rates (S-SO₄²⁻r_p) along the time course of the experimental period (Figure 3)
49
50 288 as well as a function of the total S load (figure S3a and S3b in Supplementary Material).
51
52 289 The S-SO₄²⁻r_p increased 30% between days 9 and 18 of operation. During the startup of
53
54 290 both bioreactors S-SO₄²⁻r_p progressively increased until day 24, ~~where r_p was stabilized~~
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3 291 | ~~at around up to~~ 6.5 g S-SO₄²⁻ m⁻³ h⁻¹. Besides punctual episodes, no significant impact of
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5 292 | pH was observed on S-SO₄²⁻r_p, even in the case of a pH drop to pH 5 during startup
6
7 293 | (days 14 to 18). On the contrary, S-SO₄²⁻r_p was clearly affected in PPWR on days 37
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10 294 | and 58 due to a flooding/fluidization episode (arrow A in figure 2). Finally, it is
11
12 295 | important to mention that the S-SO₄²⁻r_p drop observed in both reactors on day 64 was
13
14 296 | due to an experiment performed to evaluate the effect of an EM feeding interruption
15
16 297 | (arrow B in figure 2). ~~So~~ Consequently, the expected S-SO₄²⁻r_p drops of, ~~which were~~
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18 298 | around 13 and 42% in PPWR and PNWR, respectively, were caused by a decrease in
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21 299 | the S-SO₄²⁻ production.

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23 300 | It is worth mentioning that the S-SO₄²⁻r_p in both reactors were lower than the total S
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25 301 | loaded as H₂S and EM (figures S3a and S3b in Supplementary Material), indicating that
26
27 302 | a fraction of the S was not recovered and that was probably converted to other S species
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29 303 | such as elemental sulfur or thiosulfate. The impact of such S unbalance was more
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31 304 | noticeable in the case of the PPWR reactor in which the percentage of S-SO₄²⁻
32
33 305 | recovered was around 75-80%.

306 **Ammonia removal**

307 | No significant differences were observed between reactors in terms of NH₃ RE, which
308 | remained close to 100% all over the experimental period because of the large solubility
309 | of NH₃. However, N-species concentration in PPWR showed no evidences of nitrifying
310 | activity during the first month of operation, while slight ~~signs of~~ nitrification ~~were was~~
311 | noticed in PNWR. Simultaneously, during the first two operational weeks, a pH
312 | decrease from neutral to pH below 5 occurred in both reactors. On days 13 and 18, the
313 | HRT was reduced from 1 day to 5.7 hours (indicated in Figure 3a and 3b with arrows).
314 | Moreover, from day 28 on, pH was controlled at 7 by the permanent addition of a NaOH
315 | 0.02 g L⁻¹ solution to the make-up water line (indicated in both figures with an arrow).

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3 316 Even though neutral pH was reestablished, nitrifying activity remained almost
4
5 317 negligible. Hence, both reactors were reinoculated on day 34 to reactivate nitrification.
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7 318 ~~Right after~~Then, a gradual increase on NO_3^- production was observed. ~~Simultaneously,~~
8
9 319 while NH_4^+ concentration progressively decreased. In less than 15 days, both bioreactors
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11 320 were capable to oxidize almost all the NH_3 supplied to N-NO_3^- (Figure 3a and 3b). The
12
13 321 rest of the experimental period almost full NH_3 conversion to nitrate was achieved,
14
15 322 besides punctual days that operational failures occurred resulting in slight accumulations
16
17 323 of NH_4^+ in the liquid phase (e.g. on day 46, PNWR suffered a partial flooding of the
18
19 324 upper part of the bioreactor due to a pump pipe blockage). Besides punctual failure
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21 325 episodes suffered on days 59 and 80, a very similar behavior was observed in the PPWR
22
23 326 (Figure 3a). Nitrogen mass balances were assessed for both reactors (figure S4 in
24
25 327 Supplementary Material) showing that deviations in the N recovery oscillated between
26
27 328 20 and 55% in both reactors, with a larger dispersion in the case of the PPWR.
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331 **Butyric acid removal**

332 Butyric acid was removed almost completely ~~right~~ after the startup of both bioreactors.
333 As discussed in the next section, the high solubility of this pollutant allowed achieving
334 complete elimination during the whole experimental period.
335

336 **4 DISCUSSION**

337 Regarding ~~to~~ NH_3 removal, the nitrification capacity in both bioreactors remained
338 almost negligible during the startup phase, which was attributed to the progressive
339 acidification of the liquid phase due to SO_4^{2-} production, which led to pH values below 5
340 after 12 days of operation in both bioreactors. Characterization of packing materials

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3 341 showed a slightly acidic leachate, which was consistent with Lou and Lindsey [23] who
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5 342 reported a pH between 4.5-5 for pine wood. Slightly acid pH of woods can be related
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7 343 with resin acids content [24]. Often, buffering capacities of packing materials are not
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9
10 344 enough to compensate the production of acidic by-products from microbial oxidation in
11
12 345 the biofiltration of waste gases containing significant loads of pollutants such as H₂S or
13
14 346 VOCs. In this sense, several studies have proved that the acidification of the liquid
15
16 347 phase can negatively affect the nitrification process [6, 25-27]. Park et al. [26] proved
17
18 348 that ~~working at pH above 6.5~~ the maximal nitrification rate ~~could be~~ reduced to a
19
20 349 half ~~working at pH above 6.5, while~~. Jiang et al. [28] observed that the N-NH₄⁺ fraction
21
22 350 in the leachate (between 50 and 75%) was substantially superior than that of N-NO₂⁻ and
23
24 351 N-NO₃⁻ at pH ~~values~~ equal or above 6 due to a probable NH₄⁺ elimination by absorption
25
26 352 and reaction to (NH₄)₂SO₄. Similarly, Rabbani et al. [29] ~~achieved~~ ~~reached~~ REs over
27
28 353 90% for H₂S and NH₃ in an acidified bioreactor, ~~since because~~ the ~~stream ratio~~ H₂S/NH₃
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30 354 ~~ratio~~ permitted an effective removal of both pollutants by biological oxidation of H₂S to
31
32 355 sulfate and a subsequent chemical reaction of ammonium ~~with and~~ sulfate to form
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34 356 (NH₄)₂SO₄.
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38 357 Moreover, free ammonia (FA) and/or free nitrous acid (FNA) accumulation can inhibit
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40 358 AOB [30]. During the first two weeks of operation FA and FNA concentrations in
41
42 359 PNWR never exceeded ~~ed~~ 1.3 mg N-FA L⁻¹ and 2·10⁻⁵ mg N-FNA L⁻¹, respectively.
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44 360 ~~Considering~~ ~~i~~ Inhibitions thresholds ~~have been~~ reported by Jubany et al. [31] ~~of as~~ 5.8
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46 361 mg N-FA L⁻¹ for AOB, 0.16 mg N-FNA L⁻¹ for AOB, 0.78 mg N-FA L⁻¹ for NOB and
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48 362 0.02 mg N-FNA L⁻¹ for NOB. ~~Consequently,~~ ~~it is likely that AOB and NOB were~~
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50 363 ~~inhibited by~~ FA and/or FNA ~~inhibited AOB and NOB, particularly~~ in ~~these~~ ~~biofilter~~
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52 364 sections ~~of the bioreactors~~ closer to the inlet, where loads ~~are were~~ higher. However, no
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54 365 significant impact on the overall nitrification process was observed. Nevertheless, in
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3 366 order to decrease the FA concentration and to increase the pH, the HRT was stepwise
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5 367 decreased twice on days 13 and 18 from 24 to 5.7 hours ~~and the while a~~ permanent
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7 368 addition of a NaOH solution (0.02 g L^{-1}) was performed. These actions permitted a
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9 369 decrease of the N-NH_4^+ concentration from ~~200 $\text{mg N-NH}_4^+ \text{ L}^{-1}$~~ to $55 \text{ mg N-NH}_4^+ \text{ L}^{-1}$
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11 370 during the following 14 days of operation, while pH ~~values~~ reached neutral values.
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13 371 During the first 10 days of operation, where pH was kept at 6.5-7.0, nitrification rates of
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15 372 $0.04 \text{ g N m}^{-3} \text{ h}^{-1}$ were calculated [32] denoting ~~a certain~~ nitrifying activity.
16
17 373 However, ~~right after the pH decay,~~ N-NO_3^- production was interrupted ~~right after the pH~~
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19 374 ~~decay~~ (days 13-20). The efforts to reestablish neutral pH in the bioreactors ~~could~~ did not
20
21 375 recover the nitrifying activity ~~for~~ of PPWR, while the slight evidences of PNWR
22
23 376 nitrification capacity ~~were~~ was not enough to avoid a restart of both reactors. Hence,
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25 377 both reactors were reinoculated on day 34. Thereafter, N-NO_3^- concentration was
26
27 378 progressively increased. In approximately 15 days, most of the NH_3 supplied (3.5 ± 1.0
28
29 379 $\text{g N-NH}_3 \text{ m}^{-3} \text{ h}^{-1}$) was oxidized to NO_3^- reaching concentrations up to $50 \text{ mg N-NO}_3^- \text{ L}^{-1}$.
30
31 380 In general, N-NO_3^- production was similar in both reactors. Slight differences in pH
32
33 381 observed on day 25 onwards were attributed to the lower buffer capacity of PNWR (51
34
35 382 and $35 \text{ mL SO}_4^{2-} \text{ L}^{-1}$ for poplar and pine wood, respectively), as well as to the presence
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37 383 of resin acids in pine wood [24]. ~~However, the pH in a bioreactor is strongly influenced~~
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39 384 ~~by the acid/basic character of the pollutants supplied.~~ Furthermore, similar nitrogen
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41 385 recoveries around 40% were found in previous studies [33-35]. These deviations from
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43 386 ideality can be attributed to several facts, mainly biological processes such as
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45 387 denitrification or biomass growth. Moreover, butyric acid presence could favor
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47 388 denitrification. It is important to mention that a nitrogen mass balance carried out during
48
49 389 the entire experimental period (figure S4 in Supplementary Material) confirmed that
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51 390 almost all the ammonia supplied was biodegraded to nitrate after 30 days of operation.
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3 391 Thus, NH₃ elimination by mere adsorption onto the packing material was negligible
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5 392 considering the low loads supplied and the fact that the system operated more than 100
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7 393 days. In addition, the low adsorption capacity of packing materials under wet operating
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9 394 conditions [17] ensured that, in the long-term operation under constant loading rates,
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11 395 bioreactors were in equilibrium after a few days in terms of ad/absorption considering
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13 396 such low adsorption capacities.

16 397 In contrast with the nitrification process, sulfide oxidation showed a higher stability.

18 398 The SO₄²⁻ production increased from the beginning of the experimental period.

20 399 Concentrations close to 400 mg S-SO₄²⁻ L⁻¹ after 14 days of operation were found in

22 400 both reactors without ~~the necessity needing of~~ a selective inoculation. This fact

24 401 confirmed that the presence of sulfur-oxidizing bacteria in an aerobic sludge from a

26 402 WWTP used as inoculum, which was estimated to be around 1.5% [36], was adequate to

28 403 biodegrade H₂S to SO₄²⁻; as previously observed by Fortuny et al. [37] in a biotrickling

30 404 filter treating high H₂S loads. Previous works performing specific inoculation and

32 405 treating mixtures of H₂S and NH₃ at under similar loads and performing specific

34 406 inoculation required between 5 and 10 days to oxidize most of the H₂S to SO₄²⁻ [38-39].

36 407 In the work presented herein, the low specific surface area ~~found for of~~ both materials

38 408 (1.3 m² g⁻¹) was a handicap if compared with porous materials such as activated carbon

40 409 (950 m² g⁻¹) [40]. It is worth noticing that specific surface areas in Table 1 are referred

42 410 to the total surface area including micropores, which may be hardly available under

44 411 normal operating conditions of a biotrickling filter due to biomass growth and to the

46 412 presence of a water layer over the biofilm. Taking into account these data and

48 413 considering that no selective-specific inoculation was carried out in this study, the 7-8

50 414 days duration required observed for sulfur-sulfide oxidation to occur process, which last

52 415 around 7-8 days, were can be considered as a relatively short startup period.

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3 416 Figure 2 shows that the S-SO₄²⁻ production rate did not reach the maximal production
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5 417 during the days that the HRT was reduced although both materials showed high
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7 418 capacity to keep suitable wet conditions, ~~thus and~~ avoiding dry areas that would lead to
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9 419 poor growth and, ~~thus,~~ reduced REs. Although water holding capacities of poplar and
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11 420 pine wood are not significantly different, the water retentivity; ~~indicates-indicated~~ that
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13 421 poplar wood retains water more effectively, which beneficieate wet conditions inside the
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15 422 packing material for microorganisms maintenance (the drying rate was half of ~~that for~~
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17 423 ~~the~~ pine wood). However, although this is interesting in terms of water preservation in
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19 424 poorly watered biofilters it can be detrimental for adsorption and absorption of more
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21 425 hydrophobic pollutants such as ethylmercaptan. It is likely that ~~this the latter could be~~
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23 426 ~~one was the reason factor for which that~~ PPWR ~~was more~~ affected ~~biofilters~~
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25 427 ~~performance during~~by flooding episodes.
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29 428 Furthermore, ~~and leaving aside punctual episodes,~~ S-SO₄²⁻ production in both
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31 429 bioreactors was stabilized with the HRT set at 5.7 hours and the pH controlled in the
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33 430 range 5.9 - 7.7. In this sense, Jiang et al. [28] studied the pH effect on sulfur oxidation
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35 431 stability in a range of 4 to 8.5. ~~It was proved showing that, under all the pHs studied,~~
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37 432 over 90% of the final product was SO₄²⁻ ~~under all the pHs studied, proving the~~
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39 433 ~~robustness of this process.~~ It is important to highlight that sulfur oxidizing species able
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41 434 to develop at pHs from 1 (i.e. *Acidithiobacillus caldus* bacteria) to 10 (i.e.
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43 435 *Thioalcalivibrio* spp.) have been reported in literature [41], ~~proving the robustness of~~
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45 436 ~~this process.~~
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49 437 Regarding EM elimination, REs over 85% were reached after day 20 of operation, while
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51 438 butyric acid was almost completely removed ~~right after~~from the beginning of the
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53 439 experimental period. Probably, ~~the a difference of 5-fold times in order of~~
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55 440 ~~magnitudedifference~~ in their Henry constant (H_{EM} : $1.6 \cdot 10^{-1}$ g aq⁻¹ (gas/aqueous) and
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3 441 | $H_{\text{Butyric acid}}: 8.7 \cdot 10^{-6} \text{ g aq}^{-1}$ [9, 42]); favored butyric acid absorption in the liquid phase.
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5 442 | Total organic carbon measurements were carried out to quantify the amount of butyric
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7 443 | acid removed by mere absorption in the liquid phase or by biological activity. However,
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9 444 | ~~Measurements~~ measurements were not reliable since the detachment of the organic
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11 445 | media disguised the results. It is important to highlight that the EM removal robustness
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13 446 | is directly related to the first degradation step in which the C-S bond is broken and
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15 447 | metabolized by heterotrophic biomass. After that, the degradation pathway is the same
16
17 448 | than that corresponding to the H_2S oxidation [43]. Moreover, the acidification of both
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19 449 | bioreactors during the startup phase had surely a negative effect on EM absorption,
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21 450 | which is favored under alkaline conditions [44]. However, such an effect was not
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23 451 | observed in the present study. Arellano-García et al. [44] observed that EM solubility
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25 452 | was enhanced by around 80% by increasing the pH from 7.0 to 10.0. They considered
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27 453 | that the EC of their system was limited by the low oxidation activities of their
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29 454 | alkaliphilic microbial culture and that a pH control system was a must in order to set the
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31 455 | most suitable pH to favor the elimination of the pollutants to be treated. Furthermore,
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33 456 | EBRT studies (data not shown) suggested that the main responsible for the incomplete
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35 457 | EM elimination was ~~the~~ a mass transfer limitation, since pollutants such as mercaptans
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37 458 | require large EBRTs [12].
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43 459 | In both bioreactors no nutrients were added to the make-up water solution, since it is
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45 460 | widely accepted that most of natural organic media have enough nitrogen and
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47 461 | phosphorous content for developing a process culture [1]. Similarly, the organic matter
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49 462 | content detected (around 95% by weight) constituted an alternative substrate source for
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51 463 | biofilter microorganisms which could be used during starvation periods such as process
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53 464 | shut-downs, process rotation or intermittent loads [17].
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3 465 Since physical-chemical properties of both woods do not underscore a significant
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5 466 different behavior in terms of RE, ~~economic~~ costs associated to the ~~acquisition-purchase~~
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7 467 and ~~use-maintenance~~ of packing materials become ~~a differentiating~~ key factor. Woods
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9 468 ~~are a promising packing material for biofiltration because it is~~ a largely available and
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11 469 cost-effective resource, ~~thus becoming a promising packing material for biofiltration~~.
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14 470 Moreover, current forest management practices provide huge amounts of low-quality
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16 471 wood, which could be used in the construction of biofilters [45]. While ~~estimated~~
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18 472 ~~PNWR shows an~~ annual material costs ~~for PNWR were~~ between 10 and 16 $\text{€ m}^{-3} \text{y}^{-1}$, ~~the~~
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20 473 ~~PPWR~~ represent a ~~25% decrease of the lower~~ cost ~~was estimated for the PPWR around~~
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22 474 ~~25%~~ at the local prices of the present study (Table 1). Considering the energy to blow
23
24 475 the air through the packing material in relation to ~~the~~ pressure drop, the use of pine or
25
26 476 poplar ~~wood chips~~ represents a difference in the annual total cost of 7.3 % (Table 2).
27
28 477 Thus, ~~according to market prices in relation to materials accessibility in the zone of~~
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30 478 ~~implantation, since elimination capacities reached were similar for both woods,~~ the use
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32 479 of a kind of wood can be more attractive just ~~for because of~~ economical reasons
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34 480 ~~according to market prices in relation to materials accessibility in the zone of~~
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36 481 ~~implantation without affecting the elimination capacities reached~~. In this sense, further
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38 482 research is needed to establish materials durability based on long-term studies, which
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40 483 would be useful to perform ~~more~~ accurate suitability and economical studies with both
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42 484 packing materials.
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486 4. CONCLUSIONS

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52 487 The co-treatment of a complex mixture of NH_3 , H_2S , EM and butyric acid was
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54 488 successfully achieved in bio~~trickling filters~~~~reactors~~ packed with poplar and pine wood as
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56 489 an alternative to inorganic materials. Overall, taking all the evaluated properties into
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3 490 consideration, poplar and pine wood are support media potentially suitable to keep
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5 491 active ~~the~~ biomass growing on their surface and, subsequently, show a good
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7 492 performance in the abatement of a wide range of compounds. ~~Even though~~ Despite of
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9 493 the differences observed in the materials characterization, no significant variations in the
10
11 494 REs were observed under biofiltration conditions for the two different ~~kinds of~~ woods.
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13 495 Thus, only economical aspects such as durability and material cost, according to
14
15 496 material availability, become relevant to choose the most suitable organic ~~support~~
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17 497 mediapacking material in the case of wood supports.
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32
33 504 the Xarxa de Referència en Biotecnologia de Catalunya (XRB), Generalitat de
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35 505 Catalunya.
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41 507 **LIST OF ABBREVIATIONS**

42
43 508 **AOB** - Ammonium oxidizing bacteria

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45 509 **BET** - Brunauer Emmett and Teller

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47 510 **DMDS** - Dimethyldisulfide

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49 511 **EBRT** - Empty bed residence time

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51 512 **EC** - Elimination capacity

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53 513 **EM** - Ethylmercaptan

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55 514 **FA** - Free ammonia
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3 515 **FNA** - Free nitrous acid
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5 516 **HRT** - Hydraulic residence time
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7 517 **LR** - Loading rate
8
9 518 **NOB** - Nitrite oxidizing biomass
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11 519 **PNWR** - Pine wood reactor
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13 520 **PPWR** - Poplar wood reactor
14
15 521 **PVC** - Polyvinyl chloride
16
17 522 **RE** - Removal efficiency
18
19 523 **rp** - Production rates
20
21 524 **VOC** - Volatile organic compound
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23 525 **VSS** - volatile suspended solids
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25 526 **WWTP** - wastewater treatment plant
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27 527 **ΔP** - pressure drop
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Characterization and evaluation of poplar and pine wood in twin biotrickling filters treating a mixture of NH₃, H₂S, butyric acid and ethylmercaptan

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Abstract

Biotrickling filters for waste gas treatment are often packed with expensive, inert packing materials. In this work, poplar and pine wood chips were evaluated as low-cost packing materials in two biotrickling filters for the simultaneous treatment of a mixture of organic and inorganic volatile compounds. Bioreactors were operated at gas contact times of 22-34 s. Inlet loading rates of $3.5 \pm 1.0 \text{ gN-NH}_3 \text{ m}^{-3}\text{h}^{-1}$ and $6.5 \pm 1.1 \text{ gS-H}_2\text{S m}^{-3}\text{h}^{-1}$ were supplied, while ethylmercaptan (EM) and butyric acid were fed at loads of $3.6 \pm 1.2 \text{ g m}^{-3}\text{h}^{-1}$ and $6.0 \pm 2.1 \text{ g m}^{-3}\text{h}^{-1}$, respectively. A thorough characterization of both packing materials revealed some differences in the physical-chemical properties, mainly in their water retentivity and buffer capacity. Despite of such differences, both bioreactors performed similarly. Bioreactors were able to achieve complete removal of NH₃ and butyric acid, while H₂S and EM removal efficiencies over 90% and 70%, respectively, were found. N-species analyses in the leachate proved high nitrification rates in both biotrickling filters. Control of pH was essential for maintaining nitrification activity. Other oxidation processes were hardly affected by pH changes. Both woods showed potentially attractive as packing materials for biofiltration. Thus, availability and durability of woods are decisive factors to tip the balance.

Novelty or Significance. The work compares the performance of two biotrickling filters packed with two types of wood chips commonly used in biofilters. No previous works have directly compared the performance of two types of woods in biotrickling filters for the treatment of a range of organic and inorganic odorants because biotrickling filters are commonly packed with inert packing materials. Results indicated that the two types of woods tested behaved similarly and, more interestingly, showed equivalent treatment capacities than that of inert packing materials in the removal of a range of typical pollutants in odorant waste

gases. Research is of particular interest for improving biofiltration knowledge. In addition, this research has large practical implications in the cost-benefit of full-scale biotrickling filtration systems because inorganic packing materials commonly used in biotrickling filters are much more expensive than organic packing materials.

Keywords: Biotrickling filters, Organic media; packing characterization; odorants treatment, twin bioreactors

1 INTRODUCTION

The use of bioreactors for gaseous effluents treatment is a widely recognized biotechnology that has been successfully applied during the last decades in a wide range of industries for the abatement of a wide spectrum of pollutants. Among different configurations, biotrickling filters have demonstrated their capabilities to remove odorant pollutants in processes such as the treatment of gaseous emissions from wastewater treatment plants (WWTPs) or composting processes. However, biotrickling filters use inorganic packing materials such as plastic or ceramic beds because of the presence of a continuously flowing water phase over the packed bed. Such conditions could potentially damage organic packing materials and cause reactor flooding [1]. Regarding organic materials, the use of different types of wood chips has been reported in conventional biofilters, a bioreactor configuration without a continuous water phase flowing over the packing material [2-4]. The main advantages of wood chips as packing material are their low purchasing price, their capacity to act as water reservoir due to a high water holding capacity as well as their capacity to avoid packing material compaction [1]. Specifically, water retentivity and water holding capacity of wood chips, which are favorable in comparison to inorganic packing materials, could be beneficial during unexpected situations such as a liquid phase recirculation failure or during the treatment of extremely dry streams at high temperatures, which could end up in the packing material dry out. However, an organic material can be more rapidly exhausted and biodegraded under high water content conditions, which may hinder its

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3 67 use in biotrickling filters. The number of studies with biotrickling filters packed with
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5 68 wood chips is scarce in literature [5-6]. Chen et al. [7] studied the performance of two
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7 69 wood chips-based biofilters to reduce odor, H₂S and NH₃ from swine barn ventilation air
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10 70 distinguishing two kinds of woods: western cedar and oak wood. However, to the
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12 71 authors' knowledge there is no study indicating if a particular kind of wood is more
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14 72 effective when used in biotrickling filters. However, little attention has been paid to the
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16 73 specific characteristics of different types of woods in relation to biotrickling filters
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18 74 performance in terms of removal efficiency (RE) Less attention has been paid in trying to
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20 75 find evidences of advantages/disadvantages of using pine or poplar wood chips as
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22 76 packing materials [8]. The use of poplar and pine wood chips is highly interesting from
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24 77 an economical perspective due to their affordability and low price (45-60 € m⁻³ and 40-
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26 78 50 € m⁻³, respectively). Thus, it is interesting to study wood chips performance as
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28 79 packing material in-depth since it is an easy-to-get media, landfill disposable and a cost-
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30 80 effective material [9]. In this sense, the present work is the first work that compared twin
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32 81 biotrickling filters packed with two different woods by an exhaustive evaluation in terms
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34 82 of media characterization and bioreactors performance for the treatment of a multi-
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36 83 component gaseous stream.

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40 84 Regarding pollutants usually treated in biofilters, NH₃ and H₂S are common volatile
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42 85 inorganic compounds widely studied due to their presence in a range of sites such as
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44 86 composting plants, livestock facilities, fish processing industries or WWTPs among
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46 87 others. NH₃ concentrations up to 120 ppmv and H₂S concentrations in the range of 10-
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48 88 60 ppmv are often found in such industries [1]. EM and butyric acid are volatile organic
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50 89 compounds mainly present at low concentrations, which may only lead to a bad odor
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52 90 problem. Butyric acid has a sour, sweaty smell and belongs to hydrophilic volatile fatty
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54 91 acids group typically generated when organic matter is decomposed under anaerobic
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3 92 conditions [10]. In turn, volatile organic sulfur compounds such as ethylmercaptan (EM)
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5 93 and dimethyldisulfide (DMDS) have lately received intensive attention because of their
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7 94 very low odor threshold, high toxicity, and potential corrosive effect [11]. Specifically,
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10 95 EM is a moderately soluble in water and toxic organic compound with an odor threshold
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12 96 as low as $0.7 \mu\text{g L}^{-1}$ (0.28 ppm_v) [12]. It has been also classified as one of the most
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14 97 annoying compounds in odor emissions [13]. Overall, the complex mixture used herein
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16 98 comprises some of the most typical and most annoying pollutants released in real
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18 99 emissions. It is important to highlight that the oxygen content might not limit microbial
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21 100 biodegradation at the pollutants load typically encountered in these facilities [1].

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23 101 Based on the promising results obtained in a previous study [9], the present work
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25 102 focused on the evaluation of several properties of poplar and pine wood susceptible to
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27 103 affect the biofiltration process. In addition, this work focused on the comparison of the
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29 104 behavior of both materials under identical conditions in a biotrickling filter
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31 105 configuration treating a mixture of H₂S, NH₃, EM and butyric acid during a period of
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33 106 more than three months.
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37 38 108 **2 MATERIALS AND METHODS**

39 40 109 **2.1 Experimental setup and operating conditions of the bioreactors**

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43 110 The experimental setup consisted of two parallel PVC biotrickling filters with a height
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45 111 of 70 cm and an internal diameter of 8.6 cm. Reactors were packed with poplar and pine
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47 112 wood chips, respectively, up to a height of 50 cm, resulting in a packed bed volume of
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49 113 2.9 L per biofilter. The polluted air was supplied in up-flow mode. Inlet H₂S and NH₃
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51 114 concentrations were provided from pure gas cylinders and mixed with fresh air using
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53 115 digital mass flow controllers (Bronkhorst, The Netherlands). EM was fed by means of a
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55 116 double-head peristaltic pump (Mod. 403 U/VM2, Watson Marlow, England) that
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3 117 pumped air into glass bubblers containing liquid EM (97% purity, Sigma Aldrich,
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5 118 United States). Pure butyric acid was fed by means of a microburette Multiburette 2S
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7 119 (Crison Inst. S.A., Spain). The liquid level in both bioreactors was kept constant by
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10 120 means of two peristaltic pumps (Mod. 302 S, Watson Marlow, England) controlled by a
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12 121 home-made LabWindowsTM application. Detailed characteristics of the biofiltration
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14 122 setup can be found elsewhere [6].

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17 123 Inoculation at ambient temperature (18 - 23°C) was carried out during 48 hours in both
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19 124 reactors by continuous recirculation of an activated sludge mixture at an initial
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21 125 concentration of 1.5 g VSS L⁻¹ containing i) enriched ammonium-oxidizing bacteria
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23 126 (AOB) withdrawn from a pilot plant where partial nitrification was taking place and ii)
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25 127 aerobic sludge from a urban WWTP (Manresa, Spain). Use of aerobic sludge from
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27 128 WWTPs for inoculation is widely accepted since a wide spectrum of microorganisms is
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29 129 encountered [14-15]. A more detailed description of packing materials characteristics as
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31 130 well as the inoculation procedure of the reactors is provided in the Supplementary
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33 131 Material section S1. Several samples were extracted along the experimental period in
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35 132 order to identify sulfur-oxidizing and nitrifying bacteria. However, the organic nature of
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37 133 wood chips made difficult to obtain DNA from biofilm samples to produce reliable
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39 134 results. Thus, characterization of microbial communities in the biotrickling filters was
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41 135 not possible. Either way, an in-depth microbial characterization of biotrickling filters
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43 136 was not the scope of this work.

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48 137 Inlet concentrations of 48.5 ± 9.4 ppm_v of NH₃, 40.2 ± 3.1 ppm_v of H₂S, 11.7 ± 3.8 ppm_v
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50 138 of EM and 13.3 ± 3.4 ppm_v of butyric acid were kept constant throughout the
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52 139 experimental period, corresponding to loads of 3.5 ± 1.0 g N-NH₃ m⁻³ h⁻¹, 6.5 ± 1.1 g S-
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54 140 H₂S m⁻³ h⁻¹, 3.6 ± 1.2 g EM m⁻³ h⁻¹ and 6.0 ± 2.1 g butyric acid m⁻³ h⁻¹, respectively.
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56 141 Those are typical concentrations susceptible to be found at industrial facilities such as
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3 142 composting, food processing or WWTPs among others [1-2, 16]. During the
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5 143 experimental period, a constant gas flow rate of 310 L h⁻¹ was fed to each biofilter,
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7 144 corresponding to an initial empty bed residence time (EBRT) of 34 s. However, this
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9 145 initial value was significantly reduced in the poplar wood reactor (PPWR) due to
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11 146 operational failures. Bioreactors were operated at a room temperature of 22 ± 2°C and
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13 147 the recirculation flow rate was set at 130 mL min⁻¹. The liquid phase was continuously
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15 148 renewed by the automated supply of tap water. Make-up water flow rate varied between
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17 149 600 and 2520 mL day⁻¹, corresponding to a hydraulic residence time (HRT) between
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19 150 1.00 and 0.24 day. Thus, the Gas/Liquid ratio defined as the inlet gas flow rate divided
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21 151 by of the fresh liquid renewal varied from 12400/1 to 2953/1. The pH control was set
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23 152 from day 28 onwards by means of the permanent addition of NaOH (0.02 g L⁻¹) in the
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25 153 make-up water flow.
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32 155 **2.2 Analytical methods**

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34 156 H₂S concentration was measured using an electrochemical H₂S sensor (Sure-cell, Euro-
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36 157 Gas Management Services LTD, England) with a detection limit of 1 ppm_v. NH₃
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38 158 concentration was determined after bubbling the gas stream in acidified water and
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40 159 passed through an ammonium flow analyzer later on [17] with a detection limit of 5 mg
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42 160 N-NH₄⁺ L⁻¹. A calibrated Gas Chromatograph (6890N, Agilent Tech. S.A., Spain) was
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44 161 used for EM and butyric acid determination with a detection limit of 2 ppm_v for both
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46 162 compounds. Chloride, N-ammonium, N-nitrite, N-nitrate, S-sulfate and P-phosphate
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48 163 ions concentration in leachate samples were determined in an ICS-1000 Ion
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50 164 Chromatograph (Dionex Corp., United States) equipped with an IonPac AS9-HC
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52 165 column with a detection limit of 5 mg L⁻¹ for all species. Leachate pH and conductivity
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54 166 were measured by means of a pH 28 sensor and a MicroCM 2100 sensor (Crison Instr.
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3 167 S.A., Spain), respectively. According to the specifications of the instrumentation
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5 168 employed in this work, the following standard deviations were considered: 10% for EM
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7 169 and butyric acid RE, 1.5% for H₂S RE, 1-2% for species measured by ionic
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9 170 chromatography and 1% for the continuous flow analyzer. Regarding packing materials
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11 171 characterization, methods employed to evaluate materials properties are described
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13 172 elsewhere [18]. Finally, sulfur oxidation in bioreactors was verified through S-SO₄²⁻
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15 173 production rates, which were calculated through mass balances as detailed in the
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17 174 Supplementary Material section S2.
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23 176 **3 RESULTS**

24 177 **Packing materials characterization**

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28 178 The suitability of poplar and pine wood as packing material for biofiltration was
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30 179 evaluated by means of different physical-chemical parameters commonly studied in
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32 180 biofiltration (Tables 1 and 2). Among the natural carriers used in biofiltration, woods
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34 181 are the most extensively used together with compost, peat and soil [19]. However, the
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36 182 comparison of the behavior of different woods in biotrickling filters is still unexplored.
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38 183 Elementary analyses were performed to identify the capacity of each packing material to
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40 184 potentially provide macronutrients such as nitrogen and phosphorous necessary for
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42 185 biomass growth. Both materials presented a similar nutrient content: 46-49% C, 0.3% N,
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44 186 less than 0.1% S and 0.05% P. Concerning the specific surface area, which was
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46 187 measured by the BET technique (Table 1), wood-based materials showed a slightly
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48 188 lower specific surface area (below 1.3 m² g⁻¹) compared to compost and coconut fiber.
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50 189 A much lower specific surface area was found compared to porous materials such as
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52 190 carbons (up to 950 m² g⁻¹).
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54 191 The pH of packing materials was slightly acid (pH ≈ 6.7 for pine wood chips) while
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3 192 their buffer capacity was between 35 and 50 mL SO₄²⁻ L⁻¹ (Table 1). Sorption capacities
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5 193 were determined for both dry and wet materials to obtain information about the
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7 194 interactions nature between the contaminant, the packing materials and the aqueous
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9 195 phase. Poplar wood adsorption capacities of 0.05 and 0.06 mg toluene g⁻¹ packing
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11 196 material were achieved under dry and wet conditions, respectively, according to the
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13 197 procedure detailed in Dorado et al. [17]. Pine wood showed a 30% decrease in its
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15 198 adsorption capacity (from 0.06 to 0.04 mg toluene g⁻¹ packing material) under wet
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17 199 conditions, which are the normal operating conditions in biofilters. Larger reductions in
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19 200 the adsorption capacity under wet conditions have been reported in other packing
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21 201 materials [20]. In the materials presented herein, a lower water holding capacity and a
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23 202 similar porosity of both materials (0.88) could explain a minor reduction of such
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25 203 adsorption capacity. Moreover, the water retentivity measured, expressed as the water
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27 204 percentage lost per hour, revealed that both materials retain water efficiently. In any
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29 205 case, the maximum sorption capacity of the materials was less than 0.10 mg toluene g⁻¹
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31 206 material. The water holding capacity and water retentivity are related to packing
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33 207 materials structure. Despite the fact that water molecules can be more or less time
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35 208 retained in the material, all packing materials lose most of their water content after a
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37 209 certain period of time without the supply of extra water. For instance, when dealing with
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39 210 a dry moisture stream, it would be interesting to operate with materials with a large
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41 211 water retentivity to avoid packing material desiccation and allow microorganisms
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43 212 maintaining their activity. In the case of wood chips as unique packing material, several
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45 213 studies employing conventional biofilters achieved the highest reduction efficiencies for
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47 214 odor concentration and NH₃ removal when keeping the filter media moisture content
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49 215 over 60% (wet basis) [7,21]. Thus, both parameters were considered key factors to take
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51 216 into account when choosing the most suitable packing material for a specific scenario.
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3 217 Regarding pressure drop through the packed bed (ΔP), intrinsic ΔP for dry packing
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5 218 materials was below 1 cm water column per meter of packing material height in both
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7 219 cases (Table 2). Results agreed with typical ΔP ranges for packing materials [20].
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9 220 Interestingly, ΔP slightly increased with the presence of water inside the packing
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11 221 material even if this influence was more remarkable at higher superficial velocities (data
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13 222 not shown). In the case of poplar wood, the ΔP was twice that obtained for pine wood,
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15 223 which indicated a higher resistance to air flow due to the superficial rugosity of the
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17 224 material. Both materials were evaluated under the same water content. ΔP increased
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19 225 between 5 and 30% compared with that under dry conditions, which did not have a
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21 226 significant impact in terms of energy consumption costs as shown in Table 2. Besides
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23 227 punctual episodes, ΔP in both reactors never exceeded 7 cm of water column per meter
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25 228 of packing material height (figure S1 in Supplementary Material) during the entire
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27 229 operational period. The electricity consumption was calculated by means of a previously
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29 230 reported empirical expression $P(\text{kW}) = 3.64 \cdot 10^{-4} \cdot Q (\text{m}^3 \text{h}^{-1})$ [22] considering a
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31 231 kilowatt-hour cost of 0.08 € kWh⁻¹. The increase in the electrical consumption due to
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33 232 the ΔP was estimated according to a mechanical energy balance: $P(W) = \Delta P (\text{N m}^{-2}) \cdot Q$
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35 233 ($\text{m}^3 \text{s}^{-1}$) where P is the consumption power, ΔP is the pressure drop and Q is the
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37 234 flowrate circulating through the packing material.

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39 235 Regarding energy costs associated to blow the air through the packing material, a
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41 236 difference of 2.5% between materials was found (Table 1 and 2). Therefore, the main
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43 237 difference between packing materials laid in their purchase cost and durability. The
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45 238 purchase cost, which is directly related with the availability of each wood, had a
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47 239 significant impact in the overall costs not only because of the large volumes usually
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49 240 required for biofilter construction but also because of packing materials replacement
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51 241 due to their limited durability. Table 1 shows the purchase price of both packing
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3 242 materials according to prices of year 2014, Spanish market. The durability was
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5 243 estimated according to previous experiences of suppliers (Melcourt, UK).
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9 10 245 **Sulfur compounds removal**

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12 246 Regarding H₂S removal, both bioreactors maintained analogous trends. Initial REs
13
14 247 around 50% were measured, which increased gradually up to REs above 85% on day 13
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16 248 and remained that high the rest of the study (Figure 1a and b). Both reactors were able to
17
18 249 biodegrade H₂S to SO₄²⁻ from the beginning of the experimental period (Figure 2). Since
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20 250 unexpected situations are likely to occur during real operation, some malfunctioning
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22 251 episodes were used to evaluate the resilience capacity of wood chip-based biotrickling
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24 252 filters. Thus, EM RE varied significantly during the fluidization of the packing material
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26 253 due to a flooding episode, denoting a low capacity to face such unexpected failure.
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30 254 Both bioreactors startup took around 20 days until achieving REs above 85% (Figure 1c
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32 255 and d). Nevertheless, after reinoculation of both reactors on day 34 to reactivate the
33
34 256 nitrification process, EM REs were lower than before reinoculation. Two weeks before
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36 257 reinoculation, EM REs of 94 ± 5% and 88 ± 8% were measured for PPWR and pine
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38 258 wood reactor (PNWR), respectively. After day 34, average REs decreased down to 75 ±
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40 259 13% and 83 ± 16% for PPWR and PNWR, respectively. It is likely that flooding
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42 260 episodes in PPWR on days 37 and 58 negatively affected the EM elimination, leading to
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44 261 such significant differences in EM REs in comparison with PNWR.
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48 262 Both the startup period and unexpected operational changes lead to a significant
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50 263 dispersion of results. Despite of such variability, a similar trend was found in terms of
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52 264 EC of sulfur compounds (figure S2 in Supplementary Material). Both reactors
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54 265 performed similarly showing that the maximum EC was not reached for H₂S removal.
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56 266 However, from day 13 onwards, a pseudo-stationary period was achieved and RE values
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3 267 of $96 \pm 4\%$ and $97\% \pm 2$ were measured for PPWR and PNWR, respectively,
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5 268 corresponding to maximum EC values of 6.5 ± 0.9 and $5.6 \pm 0.6 \text{ g m}^{-3} \text{ h}^{-1}$. A plateau in
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7 269 the EC vs LR profile (figure S2b and S2d) was found at around $2 \text{ g EM m}^{-3} \text{ h}^{-1}$,
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9 270 particularly in the case of the PPWR reactor.

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11 271 Moreover, oxidation of reduced sulfur compounds was verified by assessing the S-SO₄²⁻
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13 272 production rates (S-SO₄²⁻r_p) along the time course of the experimental period (Figure 3)
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15 273 as well as a function of the total S load (figure S3a and S3b in Supplementary Material).
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17 274 The S-SO₄²⁻r_p increased 30% between days 9 and 18 of operation. During the startup of
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19 275 both bioreactors S-SO₄²⁻r_p progressively increased until day 24 up to $6.5 \text{ g S-SO}_4^{2-} \text{ m}^{-3} \text{ h}^{-1}$.
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21 276 Besides punctual episodes, no significant impact of pH was observed on S-SO₄²⁻r_p,
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23 277 even in the case of a pH drop to pH 5 during startup (days 14 to 18). On the contrary, S-
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25 278 SO₄²⁻r_p was clearly affected in PPWR on days 37 and 58 due to a flooding/fluidization
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27 279 episode (arrow A in figure 2). Finally, it is important to mention that the S-SO₄²⁻r_p drop
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29 280 observed in both reactors on day 64 was due to an experiment performed to evaluate the
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31 281 effect of an EM feeding interruption (arrow B in figure 2). Consequently, the expected
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33 282 S-SO₄²⁻r_p drops of around 13 and 42% in PPWR and PNWR, respectively, were caused
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35 283 by a decrease in the S-SO₄²⁻ production.

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37 284 It is worth mentioning that the S-SO₄²⁻r_p in both reactors were lower than the total S
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39 285 loaded as H₂S and EM (figures S3a and S3b in Supplementary Material), indicating that
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41 286 a fraction of the S was not recovered and that was probably converted to other S species
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43 287 such as elemental sulfur or thiosulfate. The impact of such S unbalance was more
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45 288 noticeable in the case of the PPWR reactor in which the percentage of S-SO₄²⁻
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47 289 recovered was around 75-80%.

54 **Ammonia removal**

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3 291 No significant differences were observed between reactors in terms of NH_3 RE, which
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5 292 remained close to 100% all over the experimental period because of the large solubility
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7 293 of NH_3 . However, N-species concentration in PPWR showed no evidences of nitrifying
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9 294 activity during the first month of operation, while slight nitrification was noticed in
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11 295 PNWR. Simultaneously, during the first two operational weeks, a pH decrease from
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13 296 neutral to pH below 5 occurred in both reactors. On days 13 and 18, the HRT was
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15 297 reduced from 1 day to 5.7 hours (indicated in Figure 3a and 3b with arrows). Moreover,
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17 298 from day 28 on, pH was controlled at 7 by the permanent addition of a NaOH 0.02 g L^{-1}
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19 299 solution to the make-up water line (indicated in both figures with an arrow). Even
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21 300 though neutral pH was reestablished, nitrifying activity remained almost negligible.
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23 301 Hence, both reactors were reinoculated on day 34 to reactivate nitrification. Then, a
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25 302 gradual increase on NO_3^- production was observed while NH_4^+ concentration
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27 303 progressively decreased. In less than 15 days, both bioreactors were capable to oxidize
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29 304 almost all the NH_3 supplied to N-NO_3^- (Figure 3a and 3b). The rest of the experimental
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31 305 period almost full NH_3 conversion to nitrate was achieved, besides punctual days that
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33 306 operational failures occurred resulting in slight accumulations of NH_4^+ in the liquid
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35 307 phase (e.g. on day 46, PNWR suffered a partial flooding of the upper part of the
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37 308 bioreactor due to a pump pipe blockage). Besides punctual failure episodes suffered on
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39 309 days 59 and 80, a very similar behavior was observed in the PPWR (Figure 3a).
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41 310 Nitrogen mass balances were assessed for both reactors (figure S4 in Supplementary
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43 311 Material) showing that deviations in the N recovery oscillated between 20 and 55% in
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45 312 both reactors, with a larger dispersion in the case of the PPWR.
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315 **Butyric acid removal**

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3 316 Butyric acid was removed almost completely after the startup of both bioreactors. As
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5 317 discussed in the next section, the high solubility of this pollutant allowed achieving
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7 318 complete elimination during the whole experimental period.
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11 320 **4 DISCUSSION**

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14 321 Regarding NH_3 removal, the nitrification capacity in both bioreactors remained almost
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16 322 negligible during the startup phase, which was attributed to the progressive acidification
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18 323 of the liquid phase due to SO_4^{2-} production, which led to pH values below 5 after 12
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20 324 days of operation in both bioreactors. Characterization of packing materials showed a
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22 325 slightly acidic leachate, which was consistent with Lou and Lindsey [23] who reported a
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24 326 pH between 4.5-5 for pine wood. Slightly acid pH of woods can be related with resin
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26 327 acids content [24]. Often, buffering capacities of packing materials are not enough to
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28 328 compensate the production of acidic by-products from microbial oxidation in the
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30 329 biofiltration of waste gases containing significant loads of pollutants such as H_2S or
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32 330 VOCs. In this sense, several studies have proved that the acidification of the liquid
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34 331 phase can negatively affect the nitrification process [6, 25-27]. Park et al. [26] proved
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36 332 that the maximal nitrification rate was reduced to a half working at pH above 6.5. Jiang
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38 333 et al. [28] observed that the N-NH_4^+ fraction in the leachate (between 50 and 75%) was
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40 334 substantially superior than that of N-NO_2^- and N-NO_3^- at pH equal or above 6 due to a
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42 335 probable NH_4^+ elimination by absorption and reaction to $(\text{NH}_4)_2\text{SO}_4$. Similarly, Rabbani
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44 336 et al. [29] reached REs over 90% for H_2S and NH_3 in an acidified bioreactor because the
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46 337 $\text{H}_2\text{S}/\text{NH}_3$ ratio permitted an effective removal of both pollutants by biological oxidation
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48 338 of H_2S to sulfate and a subsequent chemical reaction of ammonium and sulfate to form
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50 339 $(\text{NH}_4)_2\text{SO}_4$.
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3 340 Moreover, free ammonia (FA) and/or free nitrous acid (FNA) accumulation can inhibit
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5 341 AOB [30]. During the first two weeks of operation FA and FNA concentrations in
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7 342 PNWR never exceeded $1.3 \text{ mg N-FA L}^{-1}$ and $2 \cdot 10^{-5} \text{ mg N-FNA L}^{-1}$, respectively.
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9 343 Inhibitions thresholds have been reported by Jubany et al. [31] as $5.8 \text{ mg N-FA L}^{-1}$ for
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11 344 AOB, $0.16 \text{ mg N-FNA L}^{-1}$ for AOB, $0.78 \text{ mg N-FA L}^{-1}$ for NOB and $0.02 \text{ mg N-FNA L}^{-1}$
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13 345 ¹ for NOB. Consequently, FA and/or FNA inhibited AOB and NOB, particularly in
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15 346 biofilter sections close to the inlet where loads were higher. However, no significant
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17 347 impact on the overall nitrification process was observed. Nevertheless, in order to
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19 348 decrease the FA concentration and to increase the pH, the HRT was stepwise decreased
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21 349 twice on days 13 and 18 from 24 to 5.7 hours while a permanent addition of a NaOH
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23 350 solution (0.02 g L^{-1}) was performed. These actions permitted a decrease of the N-NH_4^+
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25 351 concentration from 200 to $55 \text{ mg N-NH}_4^+ \text{ L}^{-1}$ during the following 14 days of operation,
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27 352 while pH reached neutral values. During the first 10 days of operation, where pH was
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29 353 kept at 6.5-7.0, nitrification rates of $0.04 \text{ g N m}^{-3} \text{ h}^{-1}$ were calculated [32] denoting some
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31 354 nitrifying activity. However, N-NO_3^- production was interrupted right after the pH
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33 355 decay (days 13-20). The efforts to reestablish neutral pH in the bioreactors did not
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35 356 recover the nitrifying activity of PPWR, while the slight evidence of PNWR nitrification
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37 357 capacity was not enough to avoid a restart of both reactors. Hence, both reactors were
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39 358 reinoculated on day 34. Thereafter, N-NO_3^- concentration was progressively increased.
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41 359 In approximately 15 days, most of the NH_3 supplied ($3.5 \pm 1.0 \text{ g N-NH}_3 \text{ m}^{-3} \text{ h}^{-1}$) was
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43 360 oxidized to NO_3^- reaching concentrations up to $50 \text{ mg N-NO}_3^- \text{ L}^{-1}$. In general, N-NO_3^-
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45 361 production was similar in both reactors. Slight differences in pH observed on day 25
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47 362 onwards were attributed to the lower buffer capacity of PNWR (51 and $35 \text{ mL SO}_4^{2-} \text{ L}^{-1}$
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49 363 for poplar and pine wood, respectively), as well as to the presence of resin acids in pine
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51 364 wood [24]. Furthermore, similar nitrogen recoveries around 40% were found in previous
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3 365 studies [33-35]. These deviations from ideality can be attributed to several facts, mainly
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5 366 biological processes such as denitrification or biomass growth. Moreover, butyric acid
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7 367 presence could favor denitrification. It is important to mention that a nitrogen mass
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10 368 balance carried out during the entire experimental period (figure S4 in Supplementary
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12 369 Material) confirmed that almost all the ammonia supplied was biodegraded to nitrate
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14 370 after 30 days of operation. Thus, NH_3 elimination by mere adsorption onto the packing
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16 371 material was negligible considering the low loads supplied and the fact that the system
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18 372 operated more than 100 days. In addition, the low adsorption capacity of packing
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20 373 materials under wet operating conditions [17] ensured that, in the long-term operation
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22 374 under constant loading rates, bioreactors were in equilibrium after a few days in terms of
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24 375 ad/absorption considering such low adsorption capacities.

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27 376 In contrast with the nitrification process, sulfide oxidation showed a higher stability.
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29 377 The SO_4^{2-} production increased from the beginning of the experimental period.
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31 378 Concentrations close to $400 \text{ mg S-SO}_4^{2-} \text{ L}^{-1}$ after 14 days of operation were found in
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33 379 both reactors without needing a selective inoculation. This fact confirmed that the
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35 380 presence of sulfur-oxidizing bacteria in an aerobic sludge from a WWTP used as
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37 381 inoculum, which was estimated to be around 1.5% [36], was adequate to biodegrade
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39 382 H_2S to SO_4^{2-} as previously observed by Fortuny et al. [37] in a biotrickling filter treating
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41 383 high H_2S loads. Previous works performing specific inoculation and treating mixtures of
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43 384 H_2S and NH_3 under similar loads required between 5 and 10 days to oxidize most of the
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45 385 H_2S to SO_4^{2-} [38-39]. In the work presented herein, the low specific surface area of both
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47 386 materials ($1.3 \text{ m}^2 \text{ g}^{-1}$) was a handicap if compared with porous materials such as
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49 387 activated carbon ($950 \text{ m}^2 \text{ g}^{-1}$) [40]. It is worth noticing that specific surface areas in
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51 388 Table 1 are referred to the total surface area including micropores, which may be hardly
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53 389 available under normal operating conditions of a biotrickling filter due to biomass
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3 390 growth and to the presence of a water layer over the biofilm. Taking into account these
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5 391 data and considering that no specific inoculation was carried out in this study, the 7-8
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7 392 days required for sulfide oxidation to occur were considered as a relatively short startup
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10 393 period.

11 394 Figure 2 shows that the S-SO₄²⁻ production rate did not reach the maximal production
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13 395 during the days that the HRT was reduced although both materials showed high
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15 396 capacity to keep suitable wet conditions, thus avoiding dry areas that would lead to poor
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17 397 growth and reduced REs. Although water holding capacities of poplar and pine wood
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19 398 are not significantly different, the water retentivity indicated that poplar wood retains
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21 399 water more effectively, which beneficieate wet conditions inside the packing material for
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23 400 microorganisms maintenance (the drying rate was half of that for pine wood). However,
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25 401 although this is interesting in terms of water preservation in poorly watered biofilters it
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27 402 can be detrimental for adsorption and absorption of more hydrophobic pollutants such
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29 403 as ethylmercaptan. It is likely that the latter was the factor that affected biofilters
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31 404 performance during flooding episodes.

32 405 Furthermore, S-SO₄²⁻ production in both bioreactors was stabilized with the HRT set at
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34 406 5.7 hours and the pH controlled in the range 5.9 - 7.7. In this sense, Jiang et al. [28]
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36 407 studied the pH effect on sulfur oxidation stability in a range of 4 to 8.5 showing that
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38 408 over 90% of the final product was SO₄²⁻ under all the pHs studied. It is important to
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40 409 highlight that sulfur oxidizing species able to develop at pHs from 1 (i.e.
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42 410 *Acidithiobacillus caldus* bacteria) to 10 (i.e. *Thioalcalivibrio* spp.) have been reported in
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44 411 literature [41], proving the robustness of this process.

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46 412 Regarding EM elimination, REs over 85% were reached after day 20 of operation, while
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48 413 butyric acid was almost completely removed from the beginning of the experimental
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50 414 period. Probably, a 5-fold difference in their Henry constant (H_{EM} : $1.6 \cdot 10^{-1}$ g aq⁻¹

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3 415 (gas/aqueous) and $H_{\text{Butyric acid}}: 8.7 \cdot 10^{-6} \text{ g aq}^{-1}$ [9, 42]) favored butyric acid absorption in
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5 416 the liquid phase. Total organic carbon measurements were carried out to quantify the
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7 417 amount of butyric acid removed by mere absorption in the liquid phase or by biological
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9 418 activity. However, measurements were not reliable since the detachment of the organic
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11 419 media disguised the results. It is important to highlight that the EM removal robustness
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13 420 is directly related to the first degradation step in which the C-S bond is broken and
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15 421 metabolized by heterotrophic biomass. After that, the degradation pathway is the same
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17 422 than that corresponding to the H_2S oxidation [43]. Moreover, the acidification of both
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19 423 bioreactors during the startup phase had surely a negative effect on EM absorption,
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21 424 which is favored under alkaline conditions [44]. However, such an effect was not
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23 425 observed in the present study. Arellano-García et al. [44] observed that EM solubility
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25 426 was enhanced by around 80% by increasing the pH from 7.0 to 10.0. They considered
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27 427 that the EC of their system was limited by the low oxidation activities of their
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29 428 alkaliphilic microbial culture and that a pH control system was a must in order to set the
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31 429 most suitable pH to favor the elimination of the pollutants to be treated. Furthermore,
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33 430 EBRT studies (data not shown) suggested that the main responsible for the incomplete
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35 431 EM elimination was a mass transfer limitation, since pollutants such as mercaptans
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37 432 require large EBRTs [12].

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39 433 In both bioreactors no nutrients were added to the make-up water solution, since it is
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41 434 widely accepted that most of natural organic media have enough nitrogen and
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43 435 phosphorous content for developing a process culture [1]. Similarly, the organic matter
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45 436 content detected (around 95% by weight) constituted an alternative substrate source for
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47 437 biofilter microorganisms which could be used during starvation periods such as process
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49 438 shut-downs, process rotation or intermittent loads [17].
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3 439 Since physical-chemical properties of both woods do not underscore a significant
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5 440 different behavior in terms of RE, costs associated to the purchase and maintenance of
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7 441 packing materials become a key factor. Woods a largely available and cost-effective
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9 442 resource, thus becoming a promising packing material for biofiltration. Moreover,
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11 443 current forest management practices provide huge amounts of low-quality wood, which
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13 444 could be used in the construction of biofilters [45]. While estimated annual material
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15 445 costs for PNWR were between 10 and 16 € m⁻³ y⁻¹ represent a 25% lower cost was
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17 446 estimated for the PPWR at the local prices of the present study (Table 1). Considering
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19 447 the energy to blow the air through the packing material in relation to the pressure drop,
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21 448 the use of pine or poplar wood chips represents a difference in the annual total cost of
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23 449 7.3 % (Table 2). Thus, since elimination capacities reached were similar for both woods,
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25 450 the use of a kind of wood can be more attractive just because of economical reasons
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27 451 according to market prices in relation to materials accessibility in the zone of
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29 452 implantation. In this sense, further research is needed to establish materials durability
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31 453 based on long-term studies, which would be useful to perform accurate suitability and
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33 454 economical studies with both packing materials.
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41 456 **4. CONCLUSIONS**

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43 457 The co-treatment of a complex mixture of NH₃, H₂S, EM and butyric acid was
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45 458 successfully achieved in biotrickling filters packed with poplar and pine wood as an
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47 459 alternative to inorganic materials. Overall, taking all the evaluated properties into
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49 460 consideration, poplar and pine wood are support media potentially suitable to keep
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51 461 active biomass growing on their surface and, subsequently, show a good performance in
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53 462 the abatement of a wide range of compounds. Despite of the differences observed in the
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55 463 materials characterization, no significant variations in the REs were observed under
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3 464 biofiltration conditions for the two different woods. Thus, only economical aspects such
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5 465 as durability and material cost, according to material availability, become relevant to
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7 466 choose the most suitable organic packing material in the case of wood supports.
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24 474 Catalunya.
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28 476 **LIST OF ABBREVIATIONS**

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31 477 **AOB** - Ammonium oxidizing bacteria

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33 478 **BET** - Brunauer Emmett and Teller

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35 479 **DMDS** - Dimethyldisulfide

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37 480 **EBRT** - Empty bed residence time

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39 481 **EC** - Elimination capacity

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41 482 **EM** - Ethylmercaptan

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43 483 **FA** - Free ammonia

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45 484 **FNA** - Free nitrous acid

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47 485 **HRT** - Hydraulic residence time

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49 486 **LR** - Loading rate

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51 487 **NOB** - Nitrite oxidizing biomass

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53 488 **PNWR** - Pine wood reactor
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3 489 **PPWR** - Poplar wood reactor
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5 490 **PVC** - Polyvinyl chloride
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7 491 **RE** - Removal efficiency
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9 492 **rp** - Production rates
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11 493 **VOC** - Volatile organic compound
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13 494 **VSS** - volatile suspended solids
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15 495 **WWTP** - wastewater treatment plant
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17 496 **ΔP** - pressure drop
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Table 1 Physical properties, estimated prices, durabilities and annual material cost of poplar and pine wood.

Parameter	Poplar wood	Pine wood
Water-holding capacity (g g ⁻¹)	1.16	1.35
Water retentivity (% h ⁻¹)	- 0.67	-1.52
Surface area (m ² g ⁻¹)	1.21	0.99
pH	7.2	6.7
Buffer capacity (mL SO ₄ ²⁻ l ⁻¹)	51	35
Material cost (€ m ⁻³)	45-60	40-50
Estimated durability (years)	5	3-4
Annual material cost (€ m ⁻³ y ⁻¹)	9-12	10-16

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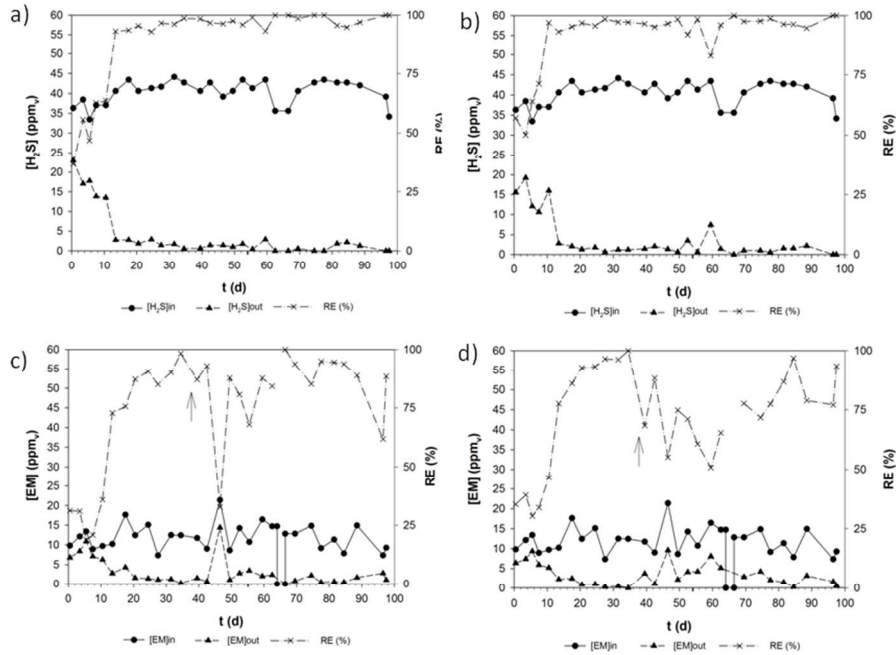


Fig. 1 Inlet and outlet H₂S concentrations and removal efficiency (RE) in the gas phase for PNWR (a) and PPWR (b). Inlet and outlet EM concentrations and removal efficiency (RE) in the gas phase in PNWR (c) and PPWR (d). Arrows indicate the reinoculation day.

Figure 1

254x190mm (96 x 96 DPI)

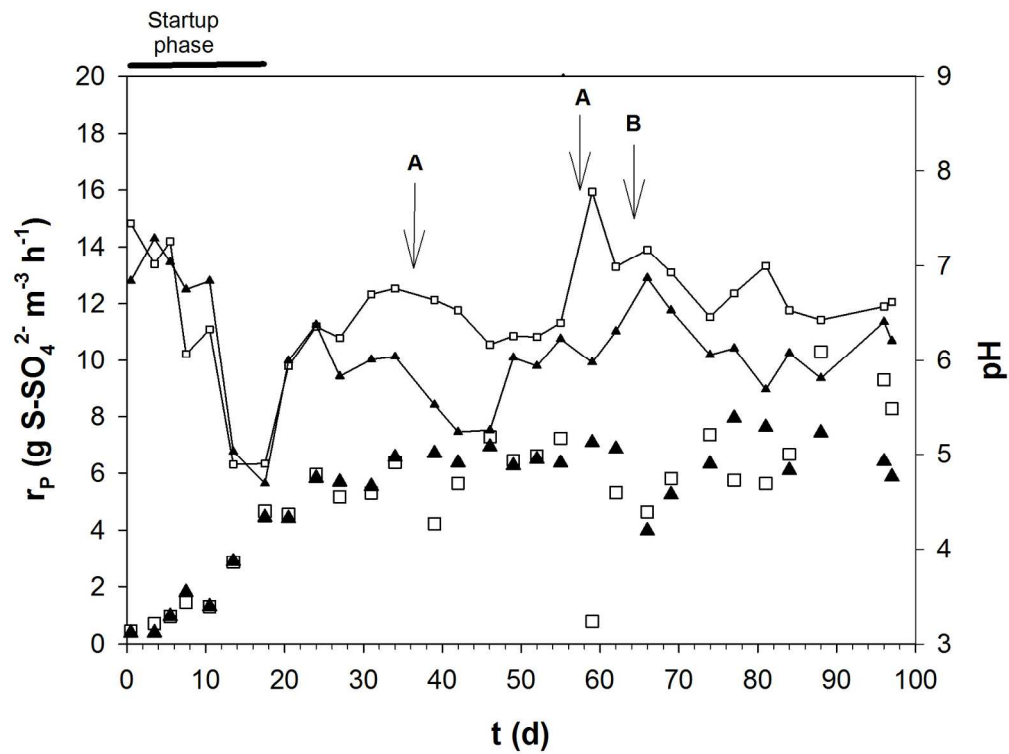


Fig. 2 Evolution of S-sulphate production rate, r_P (PPWR, \square ; PNWR, \blacktriangle) and pH in both bioreactors (PPWR, \square ; PNWR, \blacktriangle). A and B arrows are related to punctual episodes concerning PPWR and PPWR/PNWR, respectively.

Figure 2

158x126mm (300 x 300 DPI)

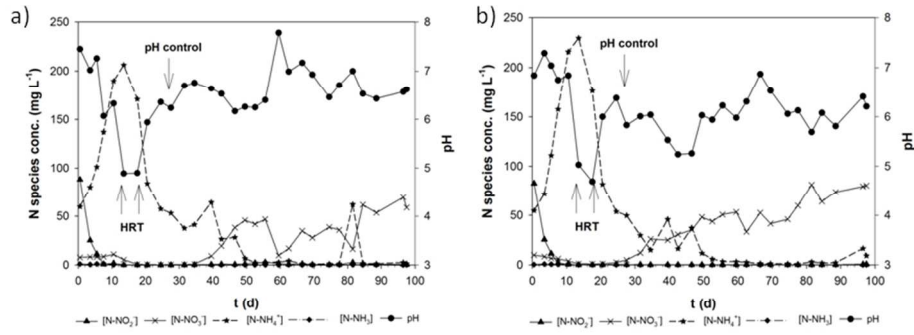


Fig. 3 Profiles of nitrogen species and pH in the liquid phase in PPWR (a) and PNWR (b).

Figure 3

254x190mm (96 x 96 DPI)