1	Performance and Feasibility of Biotrickling Filtration in
2	the Control of Styrene Industrial Air Emissions
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5 6	F. J. Álvarez-Hornos, V. Martínez-Soria, P. Marzal, M. Izquierdo, C. Gabaldón*
7	Research Group on Environmental Engineering (GI <sup>2</sup> AM), Department of Chemical
8	Engineering, Universitat de València, Av. de la Universitat s/n, 46100, Burjassot, Spain
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15	*Corresponding author. Carmen Gabaldón, Department of Chemical Engineering, Universitat
16	de València, Av. de la Universitat s/n, 46100, Burjassot, Spain. Telephone: +34963543437;
17	fax: +34963544898
18	E-mail: Carmen.gabaldon@uv.es (C. Gabaldón)
19	URLs: <u>http://www.uv.es/giam</u>
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#### 23 Abstract

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The performance and feasibility of a pilot unit of biotrickling filter (BTF) for the treatment of 25 industrial emissions polluted by styrene was investigated for one year at a fiber reinforced 26 plastic industrial site. The pilot unit was packed with a structured material with a volume of 27 0.6 m<sup>3</sup>. Monitoring results have shown successful treatment of the industrial styrene 28 emissions working at empty bed residence times (EBRT) between 31 and 66 s. The best 29 performance was obtained after 300 days when a more stable biofilm had been developed, 30 obtaining the highest elimination capacity of 18.8 g m<sup>-3</sup> h<sup>-1</sup> (removal efficiency of 75.6%) 31 working at 31 s of EBRT. In addition, a photocatalytic reactor was evaluated as pretreatment 32 of the biological process, but results have shown very low capacity for improving the BTF 33 34 performance due to catalyst deactivation. The economic feasibility of the BTF was evaluated. The total direct cost, excluding capital recovery, of the biotrickling filter technology was 35 estimated in 0.71 € year<sup>-1</sup> per Nm<sup>3</sup> h<sup>-1</sup> of treated air whereas 2.27 € year<sup>-1</sup> per Nm<sup>3</sup> h<sup>-1</sup> was 36 obtained for the regenerative catalytic oxidizer equipped with a zeolite pre-concentrator. 37 Results show that this technology is economically and environmentally competitive in 38 39 comparison with thermal treatment.

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41 Keywords: air emission, biotrickling filter, economic feasibility, pilot unit, fiber reinforced
42 plastic industry, styrene

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Styrene  $(C_8H_8)$  is a volatile organic compound (VOC) and among its chemical and 46 physical characteristics can be highlighted a vapor pressure of 0.667 kPa at 20 °C, a water 47 solubility of 300 mg L<sup>-1</sup> at 20°C and a log value of the octanol-water partition coefficient of 48 3.02. Styrene has been classified as dangerous substance with risk-phrases H226 (Flammable 49 liquid), H315 (Skin irritation), H319 (Eye irritation), H332 (Harmful if inhaled), H361d 50 (Suspected of damaging the unborn child) and H372 (Causes damage to organs through 51 prolonged or repeated exposure) (European Commission, 2002). Kuhn et al. (2000) evaluated 52 53 the ecotoxicity of styrene and it was identified as toxic to aquatic organisms, flora, fauna, soil organisms, bees and hazardous to water. Derwent et al. (1998) estimated a styrene 54 55 photochemical ozone creation potential of 14.2. Styrene is extensively used as an intermediate 56 in the chemical industry. One of the main applications is as a component of polyester resins in the fiber reinforced plastics industry that yearly produces over one million tons of composites 57 in Europe (Witten et al., 2015). In this sector, styrene evaporates from exposed uncured resin 58 59 surfaces into the atmosphere during processing until the resin is fully cured (Di Tomasso et al., 2014) resulting in waste gases characterized by high flow rates and low pollutant 60 concentrations. Nowadays, air emission regulations require techniques to treat these emissions 61 because of the adverse effects of styrene on human health (Miller et al., 1994) and its 62 classification as hazardous air pollutant (USEPA, 1994). In the control of styrene air 63 emissions, both the regenerative thermal oxidizer (RTO) and the regenerative catalytic 64 oxidizer (RCO) are the established technologies, although biological processes can be seen as 65 potential alternative to these chemical methods due to their low operational costs and lack of 66 secondary pollutant generation (Zhang et al., 2016). 67

In recent decades, styrene removal by biofiltration has been studied at laboratory by
using biofilters and biotrickling filters (Arnold et al., 1997; Dehghanzadeh et al., 2005; Novak

et al., 2008; Sempere et al., 2011). Biotrickling filter (BTF), with an aqueous stream trickling 70 71 through an inert packing material, provides advantages in comparison with conventional biofilter (BF) such as higher removal rates, lower energy consumption and smaller footprint 72 requirements (Pérez et al., 2015). In this sense, Halecky et al. (2016) compared the 73 performance of a BTF packed with Pall rings and a BF packed with Poraver media during the 74 treatment of vapors polluted with a 2:1 (wt:wt) mixture of styrene and acetone. BTF showed 75 higher removal efficiencies (REs) with a maximum styrene elimination capacity (EC) of 13 g 76 m<sup>-3</sup> h<sup>-1</sup> in comparison with 8.7 g m<sup>-3</sup> h<sup>-1</sup> of EC for the BF. Pérez et al. (2015) obtained similar 77 values of EC ~55 g m<sup>-3</sup> h<sup>-1</sup> for an inlet load (IL) ~85 g m<sup>-3</sup> h<sup>-1</sup> in a peat BF and a BTF packed 78 with polypropylene rings, both working at an empty bed residence time (EBRT) of 45 s. 79 However in terms of energy consumption, the BTF presented values of pressure drop (<59 Pa 80 m<sup>-1</sup>) substantially lower than the peat BF (around 500 Pa m<sup>-1</sup>). 81

82 Pilot studies of styrene removal are still scarce thus making difficult its industrial implementation. Lackey et al. (1998) evaluated a 1.23 m<sup>3</sup> BF packed with a mixture of pine 83 bark and composted chicken litter treating emissions polluted with styrene, methyl ethyl 84 ketone and acetone from a boat manufacturing facility. The pilot BF was tested during 13 85 months under inlet styrene concentrations varying from 0 to 380 ppm. Styrene REs greater 86 than 99% were obtained when EBRTs higher than 150 s were applied. Webster et al. (1999) 87 tested a 8 m<sup>3</sup> BTF packed with plastic spheres to control styrene emissions from a fiberglass 88 bathtub manufacturing facility. A maximum EC of 24 g m<sup>-3</sup> h<sup>-1</sup> (RE 70 – 85%) was reported 89 at inlet concentrations up to 800 mg m<sup>-3</sup> for EBRT of 86 s. Further research with pilot plant 90 studies in industrial sites are needed for demonstrating the robustness of the technology, 91 providing practical information of the performance of the process under fluctuating and 92 oscillating emissions. 93

An alternative to improve the VOC removal in biological processes can be the use of 94 photo-oxidation/photocatalytic pretreatment, which could be able to convert the VOC 95 compounds in more easily biodegradable by-products with the aim of enhancing the 96 biodegradation. Recent examples of studies combining UV photodegradation with 97 biofiltration are shown in Table 1. As it can be seen, studies have been mainly focused on 98 toluene, o-xylene and chlorinated compounds, but studies on styrene are very scarce. For 99 example, Runye et al. (2015) studied a UV photo-oxidation reactor combined with a BTF in 100 the removal of air contaminated with styrene and observed a maximum EC of 309 g m<sup>-3</sup> h<sup>-1</sup> at 101 an IL of 476 g m<sup>-3</sup> h<sup>-1</sup> working at EBRTs of 10 and 30 s in the photodegradation reactor and in 102 103 the BTF, respectively. Studies of integrating UV photocatalysis and BTF or BF treatments in the removal of styrene have not been found. 104

The scope of this work was to assess feasibility of a pilot-scale biotrickling filter in the 105 106 control of styrene air emissions emitted from a facility that manufactures fiber reinforced composite profiles and tubes. The following objectives were taken into account: (1) to 107 108 demonstrate the effectiveness and robustness of the technology under fluctuating and oscillating industrial emissions, (2) to evaluate the influence of the empty bed residence time 109 in the removal efficiency, (3) to carry out an economic feasibility study of the application of 110 111 the BTF technology in this industrial sector, and (4) to analyze the effect on the BTF performance of using an UV photocatalytic reactor as pretreatment. 112

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## 114 2. Materials and Methods

115 2.1 Pilot-scale system

The pilot-scale BTF plant which was provided by Pure Air Solutions B.V. (The Netherlands) is based on the VOCUS® Biotrickling filter system. This bioreactor design has been widely used to successfully treat VOCs or VICs in waste gases at field-scale in other

industrial sectors such are wastewater treatment plants, flexographic, automotive and wood 119 coating (Álvarez-Hornos et al., 2011; Lafita et al., 2012a, 2012b; Sempere et al., 2012). The 120 pilot plant was installed inside the factory. Figure 1 presents the scheme of the pilot BTF. The 121 biological reactor, a column with an effective volume of 0.6 m<sup>3</sup>, was packed with a structured 122 packing material (PAS Winded Media) with a 93% void fraction and 410 m<sup>2</sup> m<sup>-3</sup> of specific 123 surface area. A recirculation tank of 0.4 m<sup>3</sup> of volume was installed to collect the trickling 124 water and was equipped with a level control and fresh water was added when it was 125 necessary. A fraction of the waste gases from the factory without dilution was fed to the pilot 126 unit by using a blower equipped with a variable-frequency drive. The polluted air was 127 introduced below the column at a flow rate varying from 33 to 71 Nm<sup>3</sup> h<sup>-1</sup> and the recirculated 128 water was intermittently sprayed on the top of the filter media (counter-current mode) at a 129 flow rate of 2.7 m<sup>3</sup> h<sup>-1</sup> (spraying frequency: 10 min per h). The nutrient dosing system was 130 composed of a 100 L vessel and a dosing pump. The nutrient solution (70 g L<sup>-1</sup> of Urea, 34 g 131 L<sup>-1</sup> of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, traces of Mg, Ca, Fe, Zn, Co, Ni, Mn, Mo, B, yeast and vitamins) was 132 pumped to the recirculation tank to achieve a  $C_{loaded}/N_{supplied}$  mass ratio above 30 – 40, thus 133 assuring that nitrogen concentration in the trickling solution did not limit the biodegradation. 134 Occasionally, when the pH of the trickling solution dropped below 6.7, a control procedure 135 was carried out adding manually 40 g of NaHCO<sub>3</sub> to the recirculation tank. Around 50% of 136 the volume of the recirculation tank was partially drained and replaced with fresh water once 137 a month. The pilot unit was equipped with sensors and devices (temperature, pressure, etc.) 138 139 connected to a programmable logic controller.

The design of the photocatalytic pilot unit was based on our previous laboratory experiment treating toluene, m-xylene and n-butyl acetate at two residence times: 6 and 12 s (Palau et al., 2011). An intermediate value of 10 s was chosen for the industrial testing. The photocatalytic pilot unit consisted of a steel box (0.5 m high, 0.5 m wide and 0.75 m long).,

with a volume of 0.19 m<sup>3</sup>. The polluted air flowed through 6 panels with glass fiber 144 impregnated with TiO<sub>2</sub> catalyst and 5 stands with 5 UV lights alternative placed. A total of 25 145 commercial UV lamps (Philips® Tuv-25W, The Netherlands) with an external diameter of 28 146 147 mm and a lifetime of 9000 h were placed on the 5 stands at 0.5 cm and 7.5 cm from the panels with the catalyst. The TiO<sub>2</sub>-glass wool supported catalyst was prepared using the wash-coat 148 method. The glass wool support was impregnated with a suspension of 5% wt of TiO<sub>2</sub> 149 150 (Aeroxide P-25 from Degussa, Germany) in water. It was then dried for 1 h at 120 °C and calcined for 3 h at 350 °C. The UV lamp has a spectral output centered at a wavelength of 254 151 nm. The light intensity was 355  $\mu$ W/m<sup>2</sup> and 180  $\mu$ W/m<sup>2</sup> at 0.5 and at 7.5 cm, respectively 152 (Minolta, UV radiometer UM-10 equipped with a sensor UM-250, Japan). There was no 153 observed significant decrease in light intensity thorough the study. 154

The BTF pilot unit was running for one year in two consecutive stages. In stage I, the 155 BTF was started up and operated for 4 months at three different EBRTs: 66, 42 and 31 s with 156 157 the aim of evaluating the influence of the residence time on the removal efficiency. In stage II, the BTF pilot unit was working during 8 months under a constant EBRT of 31 s in order to 158 study the stability and the robustness of the technology. At the end of this phase, in order to 159 160 evaluate the effect of the photocatalytic reactor as pretreatment, this one was installed prior to the BTF unit. The styrene emissions were firstly treated in the photocatalytic reactor 161 (residence time of ~10 s) and then were fed to the BTF at an EBRT of 31 s. The BTF was 162 inoculated with activated sludge from the secondary clarifier of the Zuiveringsgebied-163 Oudenaarde Wastewater Treatment Plant (Oudenaarde, Belgium) without further acclimation. 164 An inoculum volume of 200 L was added to the recirculation tank and flowed during 24 h 165 through the bed with a fixed spraying frequency of 30 min per h. 166

167 The EBRT (s), RE (%), IL (g m<sup>-3</sup> h<sup>-1</sup>) and EC (g m<sup>-3</sup> h<sup>-1</sup>) were determined using the 168 equations defined below linking the inlet styrene concentration,  $C_{in}$  (g Nm<sup>-3</sup>), the outlet

styrene concentration,  $C_{out}$  (g Nm<sup>-3</sup>), the gas flow rate, Q (Nm<sup>3</sup> h<sup>-1</sup>), and the effective reactor 169 volume, V  $(m^3)$ : 170 171  $EBRT = V/Q \cdot 3600$ (1)172 173  $RE = 100 \cdot (1 - C_{out}/C_{in})$ 174 (2) 175  $IL = C_{in} \cdot Q/V$ 176 (3) 177  $EC = (C_{in} - C_{out}) \cdot Q/V$ 178 (4) 179 2.2 Analytical methods 180

Inlet and outlet gas temperatures, air flow rate, the bed pressure drop, tank levels, and 181 182 the conductivity, pH and temperature of the trickling solution were continuously monitored. Inlet and outlet total VOC concentrations were daily measured by using two photo ionization 183 detectors (PID) equipped with 10.6 eV lamps (TVOC, Ion Science Ltd., UK). The PID 184 sensors were checked and calibrated by using a total hydrocarbon analyzer equipped with a 185 flame ionization detector (Nira Mercury model 901, Spirax-Sarco, Spain) which was 186 calibrated using a synthetic standard mixture of propane (1000 ppm) in nitrogen gas 187 (Carburos Metálicos, Spain). Samples of the recirculated water were collected (twice per 188 month) to analyze chemical oxygen demand (COD), nitrogen and phosphorus content. The 189 190 identification and quantification of the main compounds presented in the waste gas emissions were carried out by collecting samples by using a GiLAir Pump (model GA-5) and activated 191 carbon tubes (type 226-09: 400-200 mg, SKC, UK) subsequently analyzed by gas 192 193 chromatography.

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### 195 **3. Results and Discussions**

196 3.1 Characterization of emissions from the facility

197 The industrial site manufactures fiber reinforced composite profiles and tubes for demanding industrial applications by pultrusion. The factory operates with continuous 8-h 198 199 work-shifts, 24 h per day, from Monday 6:00 am with shut down periods on weekends. 200 Regarding the waste gas stream, the daily average temperature of the emission varied between 16 and 30 °C, with an average of  $21.5 \pm 4.5$  °C, for the whole test period due to changes in the 201 ambient temperature at the facility between the winter and the summer seasons. A negligible 202 203 influence of this temperature variation on the removal efficiency was observed. The composition of the industrial emission was analyzed by GC from 6 samples collected during 204 205 the entire experimental period; the only organic detected compound with a remarkable 206 concentration was styrene (> 98% wt). The styrene concentrations at the waste gases were quite variable influenced by the production pattern of the factory varying from 40 to 350 mg 207 208 Nm<sup>-3</sup>. One typical styrene emission pattern over a working week is shown in Figure 2. The styrene concentrations in the waste gas emissions for the one-year experiment were classified 209 210 into three groups depending on the factory workload: low production, normal production and 211 high production (Table 2). As can be seen, the styrene concentrations in a normal production day (67% of the working period) ranged from 80 to 190 mg Nm<sup>-3</sup>. The average concentration 212 with the standard deviation for the whole data of the three groups was  $145 \pm 58$  mg Nm<sup>-3</sup>. 213

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215 3.2 Pilot plant performance

After inoculation (day 0), the BTF was operated during 4 months at three different EBRTs: 66, 42 and 31 s (Stage I). The performance of the system along this stage is shown in Figure 3, where the evolution with time of the IL and the RE is plotted. Following

inoculation, the operational conditions were selected to enhance the adaptation of the 219 220 microorganisms coming from the activated sludge inoculum to the new environment rich in styrene, so that EBRT was set at 66 s, the highest tested. A progressive increase in RE was 221 achieved during the first operational week, 75% was reached on day 8 with an IL of 16 g m<sup>-3</sup> 222  $h^{-1}$ . However, from that day the efficiency gradually decreased to ~40% on day 21, coinciding 223 with the lowest IL (~6 g m<sup>-3</sup> h<sup>-1</sup>). This fact was attributed to the low specialization of the 224 inoculum in styrene degradation since it came from an urban waste water treatment plant, thus 225 such low styrene loads didn't enhance the development of enough amount of styrene 226 degraders. In our previous experiments at laboratory, stable REs higher than 90% were 227 228 achieved since day 7 after inoculation with similar biomass and working with similar EBRT and at IL of 12 g m<sup>-3</sup> h<sup>-1</sup> (Pérez et al., 2015). The difference between the results at laboratory 229 and in the on-site testing points out that the industrial units demand a longer adaptation period 230 231 to successfully handle the fluctuating and oscillating industrial emissions. At day 28, after 7 days with ILs between 10 and 23 g m<sup>-3</sup> h<sup>-1</sup>, REs of ~70% were recovered, which could be 232 explained by a greater growth of specialized microorganisms when more amount of styrene 233 was available. From day 29 to 45 the air flow rate was increased to set an EBRT of 42 s and 234 the BTF reached an average RE of 76%  $\pm$  10% (average IL of 14  $\pm$  5 g m<sup>-3</sup> h<sup>-1</sup>) with a 235 236 maximum RE of 90% at day 37. After changing the EBRT to 31 s on day 45, an average RE of 64%  $\pm$  10% (average IL of 16  $\pm$  4 g m<sup>-3</sup> h<sup>-1</sup>) with a fluctuating efficacy between 48% (on 237 day 76 with an IL of 21 g m<sup>-3</sup> h<sup>-1</sup>) and 82% (on day 110 with an IL of 16 g m<sup>-3</sup> h<sup>-1</sup>). The 238 observed fluctuating BTF performance can be also attributed to the variability of 239 concentration in the inlet waste gas associated to the changes in the manufacturing pattern. 240

In Stage II, the EBRT was kept constant at 31 s for 8 months to study the long term performance under fluctuating and oscillating styrene emissions. As an example, the evolution with time of IL and RE is shown in Figure 4 for the last two months. The BTF

reached an average RE of 80%  $\pm$  9% with an average IL of 13  $\pm$  5 g m<sup>-3</sup> h<sup>-1</sup>. The RE varied 244 between a minimum value of 63% (on day 345 with an IL of 15.5 g m<sup>-3</sup> h<sup>-1</sup>) and a maximum 245 value of 94% (on day 306 with an IL of 11 g m<sup>-3</sup> h<sup>-1</sup>). These data are better than those 246 obtained at 31 s of EBRT 8 months ago. The average RE increased from 64% (Stage I) to 247 80% (Stage II). In addition, the RE fluctuated in greater values in Stage II (from 63% to 94%) 248 in comparison with the variation range in Stage I (from 48% to 82%). This result could be 249 attributed to the development of a more stable biofilm, with more abundance of 250 microorganism able to degrade styrene, due to the application of moderate styrene loads 251 during a long period. Similar phenomenon was observed by Webster et al. (1999) in the 252 styrene removal by a pilot BTF. In that work, by artificially increasing the styrene load, EC 253 increased from 15 g m<sup>-3</sup> h<sup>-1</sup> to 24 g m<sup>-3</sup> h<sup>-1</sup> due to the fact that more quantity of biomass was 254 established after 160 days. Therefore, biotrickling filtration seems to require a long period to 255 256 achieve a stable performance under fluctuating and discontinuous styrene emissions, being this one of special relevance for the scale-up of biotreatments from lab data. 257

Regarding the trickling water quality, it was analyzed twice per month obtaining average values of  $7.4 \pm 0.5$  of pH and  $2.4 \pm 0.8$  mS cm<sup>-1</sup> of conductivity for the whole study. Ammonium and phosphate concentrations were higher than 10 mgN L<sup>-1</sup> and 25 mgP L<sup>-1</sup>, respectively. The soluble COD concentrations kept below 100 mg L<sup>-1</sup>, thus the removed pollutant with the purge represented less than 1% of the total amount of styrene feeding, so it was assumed negligible for the evaluation of the BTF performance. The pressure drop of the bed was <20 Pa m<sup>-1</sup> for the whole experimental period.

The relationship between EC and IL at the three tested EBRT (31, 42 and 66 s) are plotted in Figure 5 (a). Data at 31 s have been drawn for Stage II. Laboratory data from previous experiment with similar operational conditions (EBRTs and IL) have been also included (Pérez et al., 2015) in Figure 5 (a) for comparative purposes. Additionally, the

variation of the RE vs the IL for the data of the pilot unit in Stage II is shown in Figure 5 (b). 269 270 The EC and RE usually decrease when the EBRT is reduced for a constant IL. From the results of this study, it can be observed an opposite trend since better results were achieved at 271 31 s (months 11 and 12 of operation) instead of at 66 s or 45 s (first two months). For 272 example, at ILs lower than 12 g  $m^{-3} h^{-1}$  near complete removal can be observed for 31 s 273 whereas REs values around 70% and between 40 and 70% were found for 42 and 66 s. 274 respectively. This behavior can be attributed to the low development of styrene degrading 275 microorganisms under industrial conditions. This lower biomass growth can also explain why 276 the outcomes of the pilot unit at 66 s differed from the lab data whereas results from both 277 278 systems matched for 31 s of residence time. For instance, the pilot unit reached an EC of 11.7  $g m^{-3} h^{-1}$  (IL of 15.6  $g m^{-3} h^{-1}$ ) versus an EC of 12.4  $g m^{-3} h^{-1}$  (IL of 13.6  $g m^{-3} h^{-1}$ ) obtained at 279 the lab at 66 s. However, quite similar performance was observed at 31 s with EC of 18.8 g m<sup>-</sup> 280 <sup>3</sup> h<sup>-1</sup> (IL of 24.9 g m<sup>-3</sup> h<sup>-1</sup>) and 17.7 g m<sup>-3</sup> h<sup>-1</sup> (IL of 23.5 g m<sup>-3</sup> h<sup>-1</sup>) for pilot and lab studies, 281 respectively. By running this long term experiment it is shown that the dynamic of growth of 282 styrene degraders plays a key role to achieve high efficiencies at industrial scale, being this 283 factor of greater importance than the contact time. 284

The results obtained in Stage II at 31 s can be considered as operational representative 285 286 data when an active biofilm has been developed, so it could be used for scale-up purposes. It can be highlighted two inlet loads for (i) removals higher than 90%, at an IL up to 12 g m<sup>-3</sup> h<sup>-1</sup> 287 with an EC of 11.2 g m<sup>-3</sup>  $h^{-1}$  (RE of 93%).; and for (ii) the highest observed elimination 288 capacity, at an IL of 24.9 g m<sup>-3</sup> h<sup>-1</sup> with an EC of 18.8 g m<sup>-3</sup> h<sup>-1</sup> (RE of 76%). Rene et al. 289 (2009) found a maximum EC of 382 g m<sup>-3</sup> h<sup>-1</sup> at an IL of 464 g m<sup>-3</sup> h<sup>-1</sup> (RE of 82%) in a 290 biofilter inoculated with the fungus Sporothrix sp. working at an EBRT of 120 s an inlet 291 concentrations ranged from 0.03 and 17.3 g m<sup>-3</sup>. The critical load depending on the EBRT 292 was 196 g m<sup>-3</sup> h<sup>-1</sup> and 260 g m<sup>-3</sup> h<sup>-1</sup> at 20 and 120 s, respectively. Although the reported 293

elimination capacity working in the laboratory were much high, this is the first study operating a BTF pilot plant at an EBRT as low as 31 s for controlling styrene at industrial air emissions. In this context, Webster et al. (1999) obtained a slightly better EC of 24 g m<sup>-3</sup> h<sup>-1</sup> (RE 70 – 85%) in a BTF pilot, but working with an EBRT threefold higher (86 s). working a BTF pilot at an EBRT threefold higher (86 s). Therefore, this would imply a three times higher bioreactor for treating similar concentrations in the waste gas emissions, which mainly depends on the manufacturing process emitting VOCs.

301 3.3 Performance of the combined system: Photocatalytic reactor and BTF pilot unit

After a year of testing, the UV photocatalytic reactor was coupled to the BTF pilot unit 302 303 as pretreatment of the styrene emissions prior to their treatment in the biological process. UV reactor and BTF were operated at a residence time of 10 and 31 s respectively. The combined 304 system was evaluated during one week and the average performance results are summarized 305 in Table 3. The combined system achieved efficiencies around 77% at IL ~16 g m<sup>-3</sup> h<sup>-1</sup>. 306 Comparing this performance with the data of the pilot unit without UV photocatalytic 307 308 pretreatment shown in Figure 5 (b), it can be seen that the combined system is within the operating variation range of the standalone BTF. This fact can be explained by the quite low 309 310 removal efficiencies obtained independently for the photocatalytic reactor, around 5%. This 311 low efficiency is in contradiction with those obtained with other aromatic compounds such toluene, xylenes or ethylbenzene (Hinojosa-Reves et al., 2012; Mohseni and Zhao, 2006; 312 Moussavi and Mohseni, 2007; Palau et al., 2012, 2011; Wei et al., 2010), for which it can be 313 considered a well-stablished technology. Results suggest that under the tested operational 314 315 conditions the TiO<sub>2</sub>-glass fiber supported catalyst was deactivated, which was corroborated by visual inspection at the end of the test (brown color appeared). Literature data confirm that the 316 by-products of the photocatalytic oxidation of styrene can block the active catalyst sites 317 (Krichevskaya and Preis, 2003). These authors found an influence of the temperature and 318

humidity on the deactivation time, with an entire restoration of the photocatalytic activity after 2 h of UV-irradiation passing clean airflow with 50% of relativity humidity due to the oxidation of the by-products. Therefore, a potential solution could be the use of an air humidification step prior to the photocatalytic reactor to enhance the oxidation of the byproduct, although more studies are necessary for evaluating this technique as pretreatment of biological processes in the fiber reinforced plastic industry.

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#### 326 3.4 Economical aspects

The economic feasibility of biotrickling filtration for the control of styrene emissions 327 in the fiber reinforced plastics industry was carried out by using a standard emission flow rate 328 of 30 000 Nm<sup>3</sup> h<sup>-1</sup> and an average styrene concentration of 145 mg Nm<sup>-3</sup>. For sizing 329 calculations, it was decided to select a safety contact time of 45 s based on the experimental 330 results of the pilot unit in which at 31 s styrene loads up to 12 g m<sup>-3</sup> h<sup>-1</sup> could be treated with 331 RE~90%. The estimations for the direct total costs excluding capital recovery are summarized 332 in Table 4. The annual costs are presented in terms of annualized cost per volumetric air flow 333 to be treated (€ year<sup>-1</sup> Nm<sup>-3</sup> h). A comparison with the regenerative catalytic oxidizer (RCO) 334 combined with a zeolite rotor as pre-concentrator step is also included in Table 4. The 335 336 installation of a zeolite rotor concentrator reduces the consumption of natural gas with a net positive impact on the viability of the thermal treatment option for diluted emissions of 337 VOCs. The electricity cost has been estimated by the power of the blower calculated from the 338 required pressure drop in each case (10 kW for the BTF and 25kW for the RCO) and with an 339 EU average electricity price of 0.12 € kWh<sup>-1</sup> (Eurostat, 2016). The consumption of natural gas 340 (energy content of 9.6 kWh Nm<sup>-3</sup>) has been calculated using an EU average price of 0.355 € 341 Nm<sup>-3</sup> (Eurostat, 2016) and an energy recovery of 95%. Capital costs of biological and thermal 342 system are similar, approximately  $1.3 - 1.5 \in$  per year and per Nm<sup>3</sup> h<sup>-1</sup> (assuming 10 years of 343

equipment life), so capital recovery has not been included for comparative purposes. Indirectannual cost, excluding capital recovery, has been estimated as 10% of the direct annual cost.

Results show that the total direct cost for the biological system, 0.71 € per year and per 346 Nm<sup>3</sup> h<sup>-1</sup>, is approximately 3 times lower than that estimated for the regenerative catalytic 347 oxidizer combined with a zeolite pre-concentrator, 2.27 € per year and per Nm<sup>3</sup> h<sup>-1</sup>. The total 348 direct cost for the BTF in this study expressed as  $1.0 \notin \text{per } 10\ 000\ \text{m}^3$  of air treated are 349 comparable to previously reported operational costs of BTF treating VOC emissions in 350 different industrial sectors. For example, Boswell et al. (2010) estimated operational costs 351 above 2 \$ per 10 000 m<sup>3</sup> of air treated in a biotreatments installed in a panel board factory. 352 Álvarez-Hornos et al. (2011) reported 2 € of operational costs per 10 000 m<sup>3</sup> of air treated in a 353 BTF treating emissions from a plastic-coating facility and Lafita et al. (2012a) obtained 354 operational cost ranging from 3 to  $10 \notin \text{per } 10\ 000\ \text{m}^3$  of air treated in a wood-coating factory. 355 356 So, biotrickling filter provides a low-cost and efficient solution for VOC control of air emissions, especially in tropical countries where there are warm temperatures that would 357 358 enhance the aerobic biodegradation.

359 **Conclusions** 

The biological removal of industrial air emissions of styrene coming from a facility 360 manufacturing fiber reinforced composite profiles was studied for one year by using a BTF 361 pilot unit. The styrene emissions exhibited variable pattern related to fluctuating and 362 discontinuous emissions with an average styrene concentration of  $145 \pm 58$  mg Nm<sup>-3</sup>. Under 363 these industrial conditions, it was necessary several months to develop a stable biofilm 364 containing enough microorganisms able to degrade styrene. Therefore, better results were 365 obtained at the last months of operation, thus being comparable with previous laboratory data 366 for the tested styrene loads. This work shows that at the lowest residence time found in 367 literature (31 s) for treating industrial air emissions of styrene 93% of removal was achieved 368

at an IL of 12 g m<sup>-3</sup> h<sup>-1</sup>. The highest elimination capacity was found on 18.8 g m<sup>-3</sup> h<sup>-1</sup> at an IL 369 of 24.9 g m<sup>-3</sup> h<sup>-1</sup>. The total direct cost, excluding capital recovery, for the BTF was estimated 370 to be 3 times lower than that for the regenerative catalytic oxidizer combined with a zeolite 371 pre-concentrator. A UV-photocatalytic reactor was tested as pretreatment of the biological 372 process. Very low efficiencies in the photoreactor occurred due to the deactivation of the 373 catalyst, thus more research on catalyst regeneration is needed for evaluating photocatalysis as 374 375 pretreatment for these industrial emissions. Spite of these results, photodegradation of VOCs, especially in tropical countries with sufficient sunlight, appears as an emergent technology 376 that could combine with biotreatments to improve the elimination capacities per unit of 377 volume. 378

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Pollutant	Pretreatment <sup>a</sup>	τ <sup>b</sup> , s	Biotreatment	<sup>a</sup> EBRT, s	Cin <sup>c</sup> ,	IL,	EC <sub>max</sub> <sup>d</sup> ,	RE, %	Reference
		,			g m <sup>-3</sup>	g m <sup>-3</sup> h <sup>-1</sup>	g m <sup>-3</sup> h <sup>-1</sup>		
Chlorobenzene	РТО	24 - 81	BF	41 – 122	0.25 – 1.5	-	60	-	Wang et al., 2009
Dichloromethane	TiO <sub>2</sub> -PCA	55.2	BTF	120	0.5 - 5.6	-	268	89	Rene et al., 2011
Dichloromethane	PTO	10	BTF	36	0.4 - 0.6	-	68.5	>66	Jianming et al., 2014
Ethylbenzene	TiO <sub>2</sub> - PCA	30	BF	30	0.5 - 7.5	450	275	61	Hinojosa-Reyes et al., 2012
n-Hexane	ZnO- PCA	60	BF	30.4	-	200	43	-	Saucedo-Lucero and Arriaga, 2014
Perchloroethylene	PTO	6 – 36	BTF	120	$5 - 45^{e}$	-	-	>99	Den et al., 2006
α-pinene	PTO	18	BTF	17	0.6 - 1.5	-	94.2	-	Cheng et al., 2011
Styrene	РТО	10	BTF	30	0.5 - 4.0	478	309	-	Runye et al., 2015
Toluene	РТО	0.5 – 1.5	BF	30 - 45	0.07 - 0.65	48	48	-	Moussavi and Mohseni, 2007
Toluene	N-TiO <sub>2</sub> /zeolite PCA	-	BF	-	0.2 - 0.5	-	-	96.7	Wei et al., 2010
Toluene	TiO <sub>2</sub> - PCA	2.7	BF	44.5	-	110	93.2	-	Palau et al., 2012
Trichloroethylene	PTO	6 – 36	BTF	120	$25 - 350^{e}$	-	-	>99	Den et al., 2006
o-Xylene	PTO	0.5 – 1.2	BF	35 - 75	-	20	20	-	Mohseni and Zhao, 2006
o-Xylene	PTO	0.5 – 1.5	BF	30 - 45	0.07 - 0.65	46	46	-	Moussavi and Mohseni, 2007

Table 1 Recent examples of VOC removal by combining UV photodegratation pretreatment with biotreatments. 

<sup>a</sup> PTO: Photoreactor, PCA: Photocatalytic reactor, BF: Biofilter, BTF: Biotrickling filter. <sup>b</sup>  $\tau$ , residence time in the photoreactor. <sup>c</sup> C<sub>in</sub>, inlet pollutant concentration. <sup>d</sup> EC<sub>max</sub>, maximum EC. <sup>e</sup> Concentrations in ppm<sub>v</sub>. 

# **Table 2** Variability of styrene concentration in the waste gases treated in the BTF pilot unit.

Factory Workload	Frequency, %	Styrene Concentration, mg Nm <sup>-3</sup>
Low production	17	40 - 80
Normal production	67	80 - 190
High production	16	190 - 350

**Table 3** Performance of the combined system (Photocatalytic reactor and BTF pilot unit).

526 Average values  $\pm$  SD.

	Combined System
IL, g m <sup>-3</sup> h <sup>-1</sup>	$15.9\pm2.2$
RE, %	$77\% \pm 5\%$
EC, g m <sup>-3</sup> h <sup>-1</sup>	$12.3 \pm 1.4$

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**Table 4** Comparison of the estimated total direct cost, excluding capital recovery, of the

530	industrial-scale BTF with the	zeolite rotor	plus RCO	configuration.
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Biotrickling filter technology	
Direct annual cost <sup>a</sup> (€ year <sup>-1</sup> Nm <sup>-3</sup> h)	
Operating labor <sup>b</sup>	0.07
Maintenance <sup>c</sup>	0.12
Utilities	
Electricity	0.29
Nutrients and chemicals	0.13
Tap water	0.03
Indirect annual cost <sup>d</sup> (€ year <sup>-1</sup> Nm <sup>-3</sup> h)	0.07
Total direct cost (€ year <sup>-1</sup> Nm <sup>-3</sup> h)	0.71
Zeolite rotor + RCO	
Direct annual cost (€ year <sup>-1</sup> Nm <sup>-3</sup> h)	
Operating labor	0.07
Maintenance	0.12
Catalyst replacement <sup>e</sup>	0.22
Utilities	
Electricity	0.72
Natural gas	0.92
Indirect annual cost (€ year <sup>-1</sup> Nm <sup>-3</sup> h)	0.22
Total direct cost (€ year <sup>-1</sup> Nm <sup>-3</sup> h)	2.27

<sup>&</sup>lt;sup>a</sup> Assumes 7,200 h year<sup>-1</sup>. <sup>b</sup> 0.5 h d<sup>-1</sup> of operator at 15 €/h + 15% of supervisor. <sup>c</sup> 0.5 h d<sup>-1</sup> of operator + 100% of maintenance labor as materials cost. <sup>d</sup> Includes overhead, administrative charges, taxes, and insurance. <sup>e</sup> 18 € m<sup>-3</sup> for metal oxide + 10% of catalyst cost as labor cost for replacing catalyst, assuming 5 years of catalyst life.

## 537 **Figure Captions**

- 538 **Figure 1** Scheme of the pilot-scale BTF.
- **Figure 2** Typical styrene emission pattern during a working week (Day 0: Monday 0:00 am).
- 540 **Figure 3** Evolution of the IL (solid triangle) and the RE (solid circle) in the BTF unit during
- 541 Stage I.
- Figure 4 Evolution of the IL (solid triangle) and the RE (solid circle) in the BTF unit duringStage II.
- 544 Figure 5 EC vs IL for different EBRTs in BTF pilot unit: 31 s (solid circle), 42 s (solid
- square) and 66 s (solid triangle); and in previous laboratory experiment: 31 s (open circle), 45
- 546 s (open square) and 60 s (open triangle).









