

1 **Performance and Feasibility of Biotrickling Filtration in**  
2 **the Control of Styrene Industrial Air Emissions**

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5 F. J. Álvarez-Hornos, V. Martínez-Soria, P. Marzal, M. Izquierdo, C. Gabaldón\*

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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: <http://www.uv.es/giam>

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23 **Abstract**

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

40

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

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## 45 **1. Introduction**

46 Styrene (C<sub>8</sub>H<sub>8</sub>) is a volatile organic compound (VOC) and among its chemical and  
47 physical characteristics can be highlighted a vapor pressure of 0.667 kPa at 20 °C, a water  
48 solubility of 300 mg L<sup>-1</sup> at 20°C and a log value of the octanol-water partition coefficient of  
49 3.02. Styrene has been classified as dangerous substance with risk-phrases H226 (Flammable  
50 liquid), H315 (Skin irritation), H319 (Eye irritation), H332 (Harmful if inhaled), H361d  
51 (Suspected of damaging the unborn child) and H372 (Causes damage to organs through  
52 prolonged or repeated exposure) (European Commission, 2002). Kuhn et al. (2000) evaluated  
53 the ecotoxicity of styrene and it was identified as toxic to aquatic organisms, flora, fauna, soil  
54 organisms, bees and hazardous to water. Derwent et al. (1998) estimated a styrene  
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  
57 the fiber reinforced plastics industry that yearly produces over one million tons of composites  
58 in Europe (Witten et al., 2015). In this sector, styrene evaporates from exposed uncured resin  
59 surfaces into the atmosphere during processing until the resin is fully cured (Di Tomasso et  
60 al., 2014) resulting in waste gases characterized by high flow rates and low pollutant  
61 concentrations. Nowadays, air emission regulations require techniques to treat these emissions  
62 because of the adverse effects of styrene on human health (Miller et al., 1994) and its  
63 classification as hazardous air pollutant (USEPA, 1994). In the control of styrene air  
64 emissions, both the regenerative thermal oxidizer (RTO) and the regenerative catalytic  
65 oxidizer (RCO) are the established technologies, although biological processes can be seen as  
66 potential alternative to these chemical methods due to their low operational costs and lack of  
67 secondary pollutant generation (Zhang et al., 2016).

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

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

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

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

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

113

## 114 **2. Materials and Methods**

### 115 2.1 Pilot-scale system

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

119 industrial sectors such are wastewater treatment plants, flexographic, automotive and wood  
120 coating (Álvarez-Hornos et al., 2011; Lafita et al., 2012a, 2012b; Sempere et al., 2012). The  
121 pilot plant was installed inside the factory. Figure 1 presents the scheme of the pilot BTF. The  
122 biological reactor, a column with an effective volume of  $0.6 \text{ m}^3$ , was packed with a structured  
123 packing material (PAS Winded Media) with a 93% void fraction and  $410 \text{ m}^2 \text{ m}^{-3}$  of specific  
124 surface area. A recirculation tank of  $0.4 \text{ m}^3$  of volume was installed to collect the trickling  
125 water and was equipped with a level control and fresh water was added when it was  
126 necessary. A fraction of the waste gases from the factory without dilution was fed to the pilot  
127 unit by using a blower equipped with a variable-frequency drive. The polluted air was  
128 introduced below the column at a flow rate varying from 33 to  $71 \text{ Nm}^3 \text{ h}^{-1}$  and the recirculated  
129 water was intermittently sprayed on the top of the filter media (counter-current mode) at a  
130 flow rate of  $2.7 \text{ m}^3 \text{ h}^{-1}$  (spraying frequency: 10 min per h). The nutrient dosing system was  
131 composed of a 100 L vessel and a dosing pump. The nutrient solution ( $70 \text{ g L}^{-1}$  of Urea,  $34 \text{ g}$   
132  $\text{L}^{-1}$  of  $(\text{NH}_4)_2\text{HPO}_4$ , traces of Mg, Ca, Fe, Zn, Co, Ni, Mn, Mo, B, yeast and vitamins) was  
133 pumped to the recirculation tank to achieve a  $C_{\text{loaded}}/N_{\text{supplied}}$  mass ratio above 30 – 40, thus  
134 assuring that nitrogen concentration in the trickling solution did not limit the biodegradation.  
135 Occasionally, when the pH of the trickling solution dropped below 6.7, a control procedure  
136 was carried out adding manually 40 g of  $\text{NaHCO}_3$  to the recirculation tank. Around 50% of  
137 the volume of the recirculation tank was partially drained and replaced with fresh water once  
138 a month. The pilot unit was equipped with sensors and devices (temperature, pressure, etc.)  
139 connected to a programmable logic controller.

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

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

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

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<sub>in</sub> (g Nm<sup>-3</sup>), the outlet

169 styrene concentration,  $C_{out}$  ( $\text{g Nm}^{-3}$ ), the gas flow rate,  $Q$  ( $\text{Nm}^3 \text{h}^{-1}$ ), and the effective reactor  
170 volume,  $V$  ( $\text{m}^3$ ):

171

$$172 \quad EBRT = V/Q \cdot 3600 \quad (1)$$

173

$$174 \quad RE = 100 \cdot (1 - C_{out}/C_{in}) \quad (2)$$

175

$$176 \quad IL = C_{in} \cdot Q/V \quad (3)$$

177

$$178 \quad EC = (C_{in} - C_{out}) \cdot Q/V \quad (4)$$

179

## 180 2.2 Analytical methods

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



194

### 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  
198 demanding industrial applications by pultrusion. The factory operates with continuous 8-h  
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  
201 16 and 30 °C, with an average of  $21.5 \pm 4.5$  °C, for the whole test period due to changes in the  
202 ambient temperature at the facility between the winter and the summer seasons. A negligible  
203 influence of this temperature variation on the removal efficiency was observed. The  
204 composition of the industrial emission was analyzed by GC from 6 samples collected during  
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  
207 quite variable influenced by the production pattern of the factory varying from 40 to 350 mg  
208  $\text{Nm}^{-3}$ . One typical styrene emission pattern over a working week is shown in Figure 2. The  
209 styrene concentrations in the waste gas emissions for the one-year experiment were classified  
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  
212 day (67% of the working period) ranged from 80 to 190  $\text{mg Nm}^{-3}$ . The average concentration  
213 with the standard deviation for the whole data of the three groups was  $145 \pm 58$   $\text{mg Nm}^{-3}$ .

214

#### 215 3.2 Pilot plant performance

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

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

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

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

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

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

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

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

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

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

302 After a year of testing, the UV photocatalytic reactor was coupled to the BTF pilot unit  
303 as pretreatment of the styrene emissions prior to their treatment in the biological process. UV  
304 reactor and BTF were operated at a residence time of 10 and 31 s respectively. The combined  
305 system was evaluated during one week and the average performance results are summarized  
306 in Table 3. The combined system achieved efficiencies around 77% at IL  $\sim 16 \text{ g m}^{-3} \text{ h}^{-1}$ .  
307 Comparing this performance with the data of the pilot unit without UV photocatalytic  
308 pretreatment shown in Figure 5 (b), it can be seen that the combined system is within the  
309 operating variation range of the standalone BTF. This fact can be explained by the quite low  
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  
312 toluene, xylenes or ethylbenzene (Hinojosa-Reyes et al., 2012; Mohseni and Zhao, 2006;  
313 Moussavi and Mohseni, 2007; Palau et al., 2012, 2011; Wei et al., 2010), for which it can be  
314 considered a well-established technology. Results suggest that under the tested operational  
315 conditions the  $\text{TiO}_2$ -glass fiber supported catalyst was deactivated, which was corroborated by  
316 visual inspection at the end of the test (brown color appeared). Literature data confirm that the  
317 by-products of the photocatalytic oxidation of styrene can block the active catalyst sites  
318 (Krichevskaya and Preis, 2003). These authors found an influence of the temperature and

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

325

### 326 3.4 Economical aspects

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

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

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

## 359 **Conclusions**

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

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

379

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381

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389



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423 [tricity\\_prices\\_for\\_industrial\\_consumers](http://ec.europa.eu/eurostat/statistics-explained/index.php/Energy_price_statistics#Electricity_prices_for_industrial_consumers). (accessed 7.15.16).

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514

515 **Table 1** Recent examples of VOC removal by combining UV photodegradation pretreatment with biotreatments.

| Pollutant         | Pretreatment <sup>a</sup>       | $\tau^b$ , s | Biotreatment <sup>a</sup> | EBRT, s  | $C_{in}^c$ ,<br>$g\ m^{-3}$ | IL,<br>$g\ m^{-3}\ h^{-1}$ | $EC_{max}^d$ ,<br>$g\ m^{-3}\ h^{-1}$ | RE, % | Reference                        |
|-------------------|---------------------------------|--------------|---------------------------|----------|-----------------------------|----------------------------|---------------------------------------|-------|----------------------------------|
| Chlorobenzene     | PTO                             | 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 <sup>e</sup>         | -                          | -                                     | >99   | Den et al., 2006                 |
| $\alpha$ -pinene  | PTO                             | 18           | BTF                       | 17       | 0.6 – 1.5                   | -                          | 94.2                                  | -     | Cheng et al., 2011               |
| Styrene           | PTO                             | 10           | BTF                       | 30       | 0.5 – 4.0                   | 478                        | 309                                   | -     | Runye et al., 2015               |
| Toluene           | PTO                             | 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 <sup>e</sup>       | -                          | -                                     | >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       |

516 <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>  $C_{in}$ , inlet  
517 pollutant concentration. <sup>d</sup>  $EC_{max}$ , maximum EC. <sup>e</sup> Concentrations in ppm<sub>v</sub>.

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521

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

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

523

524



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

526 Average values  $\pm$  SD.

| <b>Combined System</b>              |                |
|-------------------------------------|----------------|
| IL, $\text{g m}^{-3} \text{h}^{-1}$ | $15.9 \pm 2.2$ |
| RE, %                               | $77\% \pm 5\%$ |
| EC, $\text{g m}^{-3} \text{h}^{-1}$ | $12.3 \pm 1.4$ |

527

528

529 **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.

| <b>Biotrickling filter technology</b>                                       |             |
|---|-------------|
| 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)                 | <b>0.71</b> |
| <b>Zeolite rotor + RCO</b>  |             |
| 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)                 | <b>2.27</b> |

531 <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 +  
 532 100% of maintenance labor as materials cost. <sup>d</sup> Includes overhead, administrative charges, taxes, and  
 533 insurance. <sup>e</sup> 18 € m<sup>-3</sup> for metal oxide + 10% of catalyst cost as labor cost for replacing catalyst,  
 534 assuming 5 years of catalyst life.

535

536

537 **Figure Captions**

538 **Figure 1** Scheme of the pilot-scale BTF.

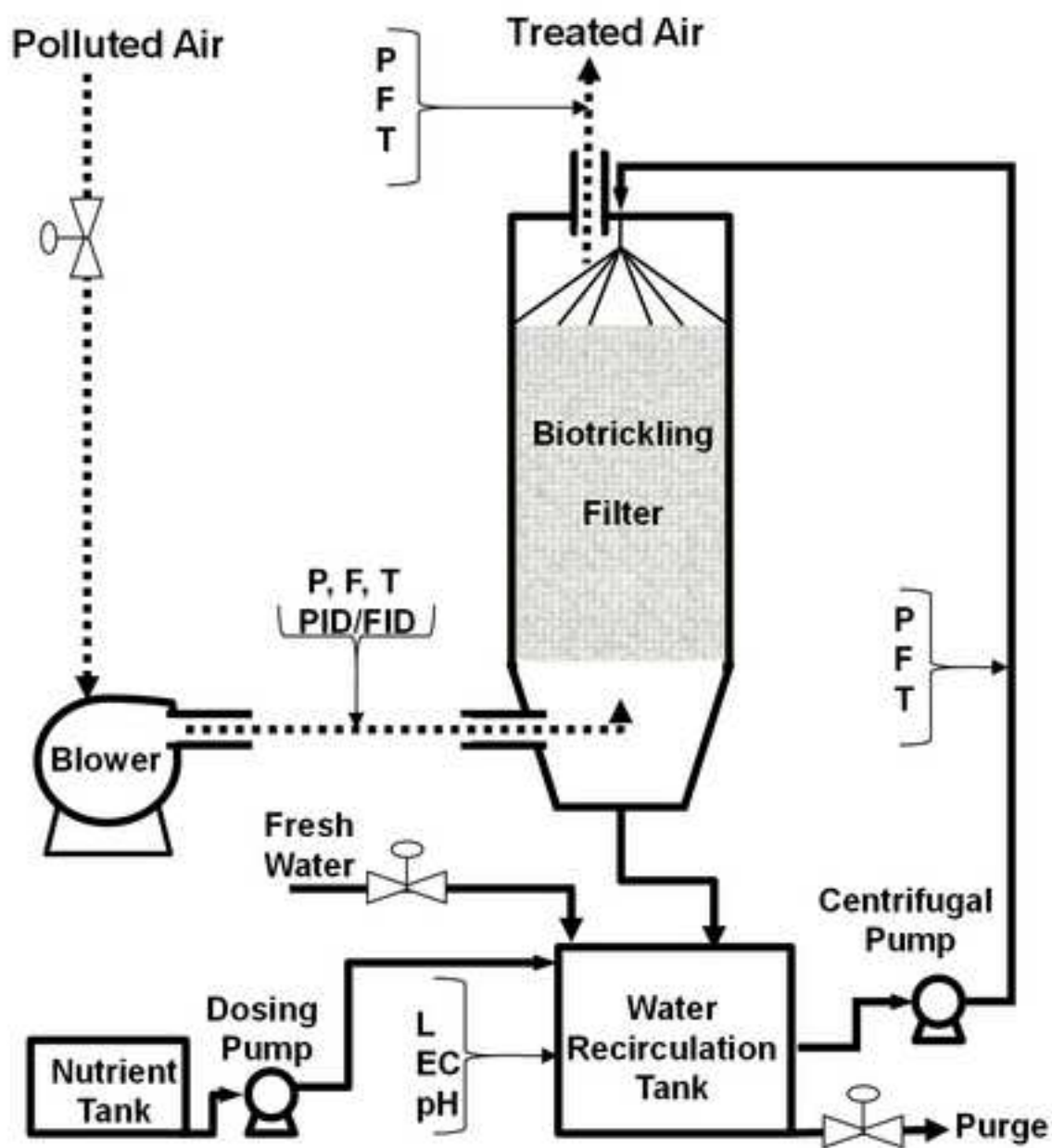
539 **Figure 2** Typical styrene emission pattern during a working week (Day 0: Monday 0:00 am).

540 **Figure 3** Evolution of the IL (solid triangle) and the RE (solid circle) in the BTF unit during  
541 Stage I.

542 **Figure 4** Evolution of the IL (solid triangle) and the RE (solid circle) in the BTF unit during  
543 Stage II.

544 **Figure 5** EC vs IL for different EBRTs in BTF pilot unit: 31 s (solid circle), 42 s (solid  
545 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).

Figure1



**Specification:**

- P: Pressure Detector (Pa)
- T: Temperature Detector ( $^{\circ}\text{C}$ )
- F: Flowrate Measurer ( $\text{m}^3/\text{h}$ )
- PID/FID: VOC Concentration ( $\text{mg C}/\text{m}^3$ )
  - PID: Photo Ionization Detector
  - FID: Flame Ionization Detector
- L: Liquid Level Detector
- EC: Electrical Conductivity Detector

— Water line  
..... Air line

Figure2

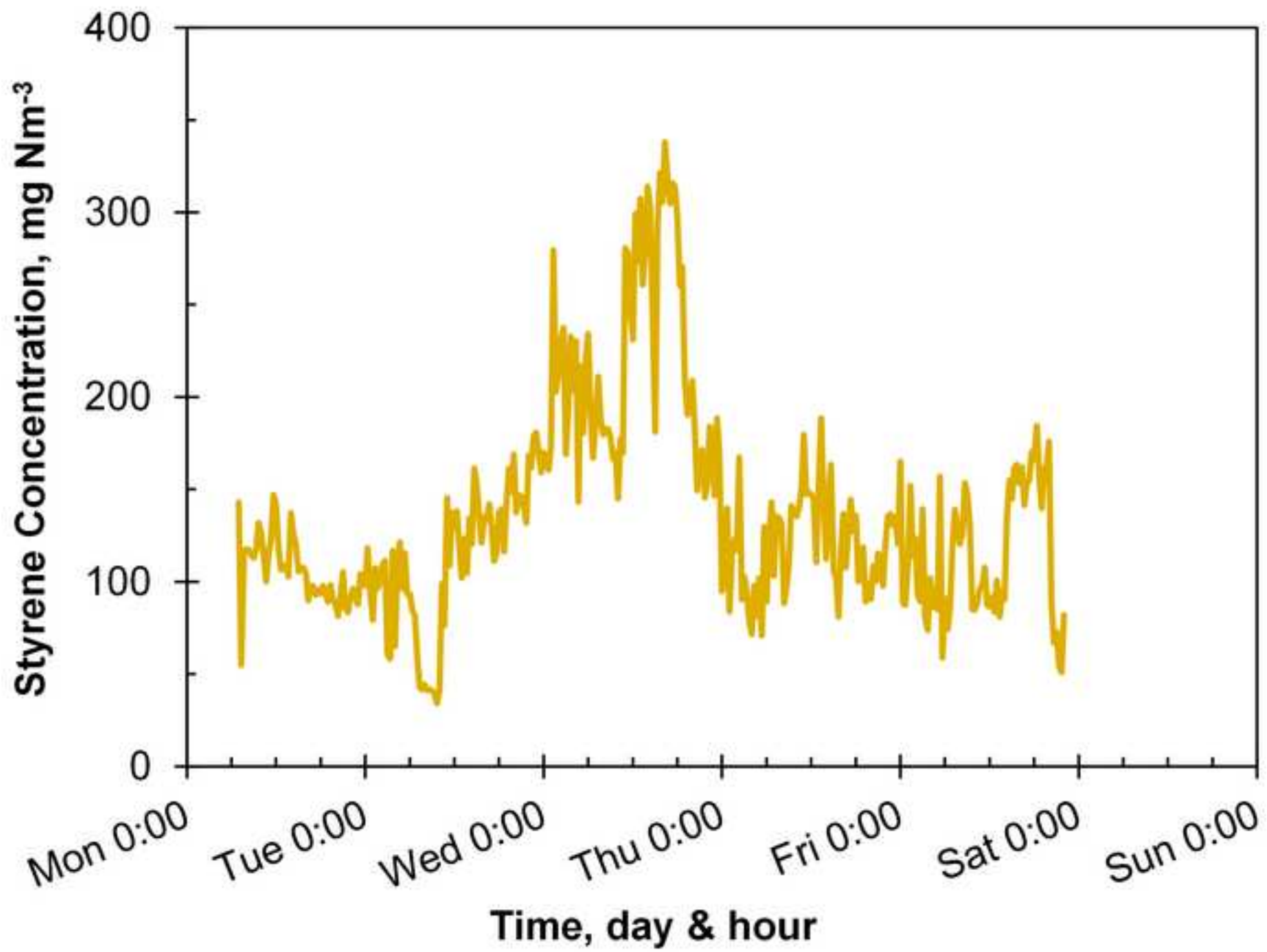


Figure3

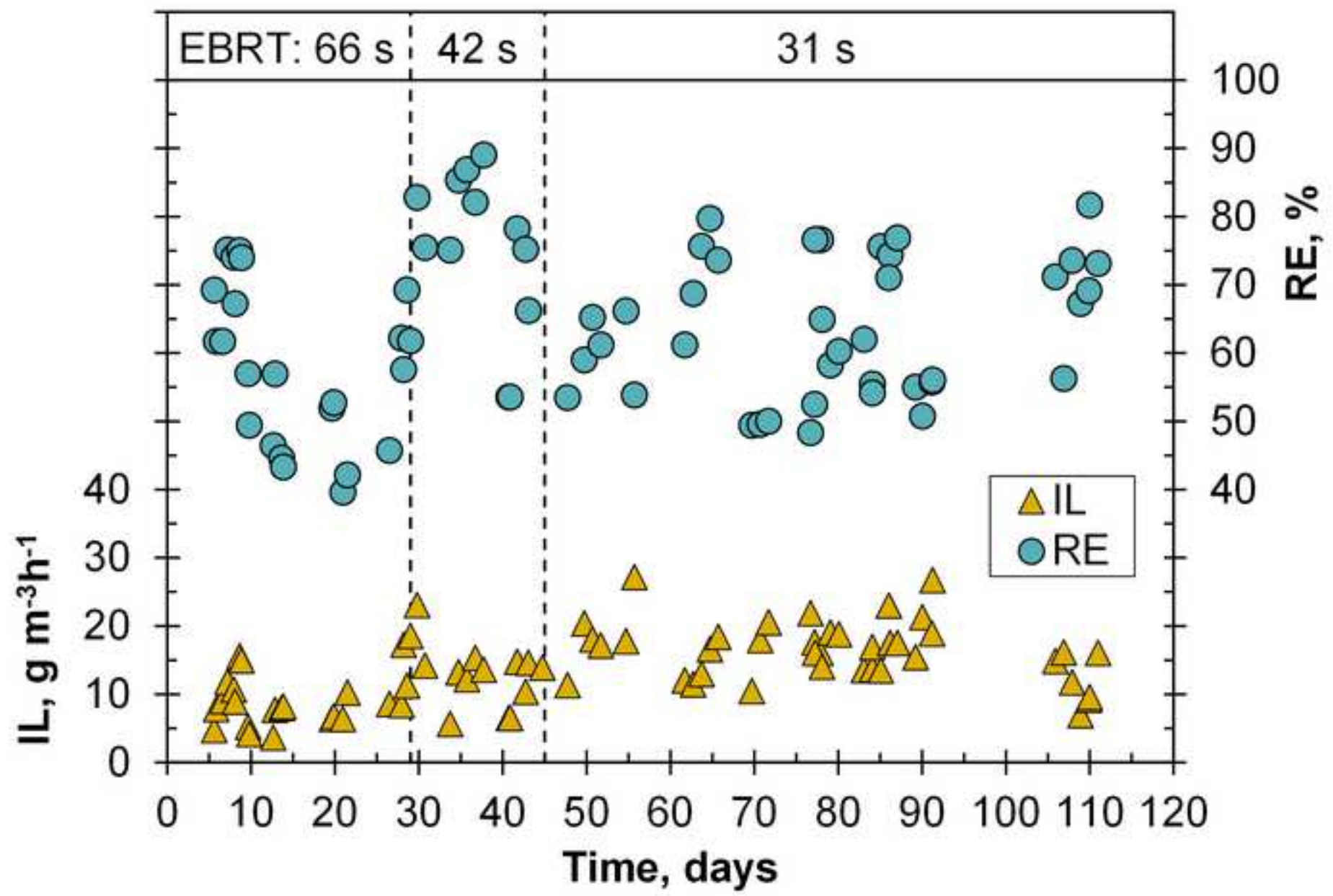


Figure4

