Enhanced styrene removal in a two-phase partitioning bioreactor operated as a biotrickling filter: towards full-scale applications

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Abstract

Styrene vapor abatement was investigated in a two-phase partitioning bioreactor operated as a biotrickling filter (TPPB-BTF). The removal performance of the TPPB-BTF was simultaneously compared with a conventional BTF, which served as a control. Industrial-grade silicone oil was used as the non-aqueous phase in the TPPB-BTF due to its high affinity for styrene. Both bioreactors were operated at styrene inlet concentrations ranging from 55 to 323 mg C m^{-3} and empty bed residence times (EBRT) of 15 – 30 s, corresponding to pollutant loading rates of 13 – 77 g C m^{-3} h^{-1}. Both bioreactors exhibited styrene removal efficiencies (REs) higher than 90% at an EBRT of 30 s. Nevertheless, the TPPB-BTF showed a superior removal performance than that recorded in the control BTF at EBRTs shorter than 30 s. REs of 89%, 84% and 57% were recorded in the TPPB-BTF at EBRT of 15 s and loading rates of 13, 22 and 77 g C m^{-3} h^{-1}, respectively, while the control BTF supported removal efficiencies of 64%, 42% and 18-42% under the same experimental conditions. The resilience and robustness of the TPPB-BTF over styrene shock loadings and transient inlet concentration was also confirmed, the TPPB-BTF being able to recover a stable RE of 89% one day after such operation disturbances. The potential of the TPPB-BTF towards full scale applications was also critically discussed based on the experimental determination of silicone oil loses through aqueous phase renewal, which accounted for 0.4% of the initial volume of oil added to the TPPB-BTF after 87 days of operation.

Keywords: Biological air treatment; Biotrickling filtration; Silicone oil; Styrene; Two-phase partitioning bioreactor.

1. Introduction

Styrene is an aromatic volatile organic compound (VOC) used in the chemical industry for the production of polystyrene, styrene copolymers and polyester resins [1]. Styrene is therefore a commodity chemical used extensively in the manufacture of a wide variety of commercial products such as plastics, paints, coatings and synthetic rubbers [2]. Due to its volatility (vapor pressure of 0.6 kPa at 20ºC) and massive use, styrene is also a major air pollutant [3,4]. Exposure to styrene may produce irritation of the skin, eyes, and respiratory tract; depression of the central nervous system; headache; fatigue and nausea [5]. Moreover, although evidence is limited up to date, occupational studies have shown styrene to be a suspected carcinogen [6]. Styrene abatement in industrial emissions is difficult to achieve owing to its low average concentration in the exhaust gases, which are not expected to exceed 424 mg C m^{-3} as this is the recommended threshold limit value for humans [3,7]. In this regard, physical-chemical technologies for air treatment (e.g. absorption, adsorption and thermal/catalytic oxidation) have been progressively replaced by biotechnologies, which present lower operational costs, energy requirements and environmental impacts [1,4,8,9]. Despite the advantages of biotechnologies over their physical-chemical counterparts, the poor aqueous solubility of styrene and its toxicity towards microbial communities still represent a challenge for the development of highly-efficient and compact bioreactors [7,9–11].

Two-phase partitioning bioreactors (TPPBs), based on the addition of a non-aqueous phase, have been reported as a good alternative for the treatment of air pollutants exhibiting both poor aqueous solubility and toxicity [12]. In particular, TPPBs using silicone oil as a non-aqueous phase (NAP) were successfully used for styrene removal in batch tests [7,13]. Although these batch studies performed in stirred tanks lacked of a practical application for the treatment of industrial waste gases, the enhanced performance of TPPBs over controls without silicone oil was confirmed. The improved styrene removal in TPPBs was attributed to the high solubility of styrene in silicone oil, which is ~250 times higher than that in water (air/silicone oil partition coefficient of 0.00044) [9]. TPPBs operated as biotrickling filters (BTFs) were recently investigated for the treatment of styrene [10,11]. The ease of temperature/pH control and a low pressure drop along the packed bed were highlighted as key features encouraging the operation of TPPBs as BTFs [10]. In this regard, industrial BTFs are mostly operated with intermittent liquid recycling and packed with inorganic materials with a high void fraction to minimize the pressure drop (energy saving) and clogging issues in the long-term operation [4,14–16]. Unfortunately, no systematical studies on styrene removal in TPPBs considering such industrial operating conditions are available in the literature.

The aim of this work was to investigate the styrene removal performance of a TPPB operated as a BTF under typical industrial conditions (steady and transient conditions). For the first time, industrial-grade silicone oil rather than analytical-grade oil was used for styrene removal in a TPPB. Air flow rates yielding empty bed residence times (EBRT) of 15-30 s were investigated, which are the target EBRT values in full-scale BTFs treating styrene. The steady performance of the TPPB-BTF achieved at several styrene loadings was compared with a control BTF without silicone oil.

2. Materials and methods

2.1. Chemicals and mineral salt medium

All chemicals for mineral salt medium (MSM) preparation were purchased from VWR with a purity of at least 99%. Industrial-grade silicone oil (XIAMETER PMX-200) characterized by kinematic viscosity and density of 50 cSt and 0.96 g mL^{-1} at 25ºC, respectively, was obtained from Dow Corning (Univar, Spain). A silicone oil percentage of 5% $^{v}/_{v}$ relative to the BTF packed volume was used.

The MSM was composed of (g L^{-1}): NH_4Cl, 9.7; $MgSO_4 \cdot 7H_2O$, 0.9; $(NH_4)_2HPO_4$, 2.2; $NaHCO_3$, 0.5; NaOH, 0.4; KCl, 0.6; and 24 mL L^{-1} of a micronutrient solution containing (g L^{-1}): 0.53 $CaCl_2$, 0.2 $Fe_2(SO_4)_3$, 0.01 $ZnSO_4 \cdot 7H_2O$, 0.01 $CoCl_2 \cdot 6H_2O$, 0.004 $MnCl_2 \cdot 4H_2O$, 0.003 $Na_2MoO_4 \cdot 2H_2O$, 0.1 $NiSO_4 \cdot 6H_2O$, 0.01 H_3BO_3 and vitamins at trace concentrations. The final pH of the medium was adjusted to 8.

2.2 Inoculum

Five glass bottles of 0.6 L total volume were provided with 200 mL of silicone oil, 90 mL of MSM and 10 mL of fresh activated sludge (secondary recycling sludge from a municipal WWTP). The bottles were gas-tight closed with butyl septa and plastic rings. Then, 5 µL of styrene were injected. The bottles were cultured at 25ºC under magnetic mixing of 300 rpm. In order to enrich the system with hydrophobic biomass able to growth immersed in silicone oil (or on the NAP/water interface), the aqueous phase was renewed by fresh MSM each styrene depletion cycle during a total enrichment period of 60 days (styrene depletion cycles of 7-15 days). This microbial enrichment methodology for TPPB inoculation has been reported as suitable for the removal of hydrophobic air pollutants [17] . The TPPB-BTF was inoculated with both 1 L of silicone oil and 0.45 L of MSM from the bottles above described. The control BTF without silicone oil was inoculated with 1 L of activated sludge from the secondary recycling sludge from municipal WWTP.

2.3 Experimental setup

Styrene removal was carried out in two identical lab-scale biotrickling filters: BTF (control without NAP) and TPPB-BTF (provided with 5% NAP relative to the packed bed volume). Each bioreactor consisted of cylindrical methacrylate columns (0.144 m inner diameter, 1.63 m height) with a working packed volume of 20 L coupled to an external recirculation tank of 6 L working volume (Fig. 1). Both TPPB-BTF and BTF were operated in countercurrent flow mode at room temperature. Polypropylene rings (Flexiring®, Koch-Glitsch B.V.B.A., Belgium) of 25 mm nominal diameter and a surface area of 207 m^2 m^{-3} was used as the packing material, which is similar to those used in industrial BTF applications [18]. The polypropylene rings had a void fraction of 92% and bulk density of 71 kg m^{-3} (data provided by the supplier). The liquid phase was recycled at a rate of 10 m h^{-1} from the 10-L holding tank by a centrifugal pump. The air stream was laden with styrene by using a syringe pump (New Era, NE 1000 model, USA). The gas flow rate was adjusted by using a mass flow controller (Bronkhorst Hi-Tec, the Netherlands). The liquid phase in both bioreactors was controlled to pH 8 by periodical additions of $NaHCO_3$, while the ammonium concentration in the liquid phase was maintained above 10 mg L^{-1} in the holding tank. Aqueous NH_4^+, PO_4^{3-} and total organic carbon (TOC) were periodically measured in both bioreactors. Silicate (SiO_2) concentration in the aqueous phase of the TPPB-BTF was periodically analyzed to determine potential silicone oil loses during aqueous phase renewal.

<Figure 1>

2.4 Operating conditions

Both BTF and TTPB-BTF were operated in parallel in order to compare their performance. The experimental time was divided in three operating phases, simulating real-case styrene emissions. The operating conditions set in both BTFs are summarized in Table 1. In brief, phase A (days 0-5) was characterized by a continuous liquid recycling in order to promote the biomass adhesion on the packing material. In phase B (days 6-60), the styrene removal efficiency (RE, %) and elimination capacity (EC, g C $m_{reactor}^{-3}$ h^{-1}) of both systems was investigated at several empty bed residence times (EBRT), while maintaining an average styrene inlet concentration of ~184 mg C m^{-3}. From phase B on, the liquid recycling was set to operate intermittently for 15 min every 2 h. In phase C (days 61-75), the removal performance at several styrene inlet concentrations, while maintaining an EBRT of 15 s, was investigated. Increasing inlet concentrations from 55 mg C m^{-3} up to 323 mg C m^{-3} were applied in this phase, yielding inlet loadings (ILs) from 13 to 77 g C m^{-3} h^{-1}. Transient styrene inlet concentrations were tested in the TPPB-BTF in order to evaluate its removal performance under fluctuating conditions typically found in industrial emissions. For this purpose, styrene inlet concentrations of 92, 184, 323, 415, 553 and 645 mg C m^{-3} were evaluated. Finally, the conditions set in days 37-47, corresponding to EBRT of 20 s and inlet styrene concentration of 184 mg C m^{-3}, were restored in the TPPB-BTF for 20 days to evaluate the removal performance after the transient conditions. 3 L of aqueous phase of both bioreactors was renewed every 7 days by fresh MSM. The aqueous phase renewal in the TPPB-BTF was done as follows: once a liquid recycling cycle finished (15 min every 2 hours), the aqueous phase was allowed to separate from the silicone oil layer for 1 h. Then, the aqueous phase was drained from the bottom of the tank to avoid silicone oil losses.

<Table 1>

2.5 Analytical methods

The styrene concentration was measured online using two total hydrocarbon analyzers (Nira Mercury 901, Spirax Sarco, Spain). The CO_2 concentration was analyzed using a CARBOCAP® GM70 dioxide analyzer (Vaisala, Finland). Pressure drop was periodically measured with a MP101 manometer (KIMO, Spain). The conductivity and pH were measured daily (WTW, pH/Cond 340i, Germany). NH_4^+ and PO_4^{3-} concentrations were quantified daily using Merck MQuant® test strips 110024 and 110428, respectively. TOC was measured with a total organic carbon analyzer for liquid samples (TOC-VCHS, Shimadzu, Japan). SiO_2 concentration was determined with a Merck Spectroquant® kit (Code 100857).

3. Results and discussion

3.1. Removal performance of the control BTF without silicone oil

The biomass in the control BTF, inoculated with fresh activated sludge, was attached on the packing material within the first 5 days of continuous liquid recycling. From day 6 on, intermittent liquid recycling was set and the removal performance progressively increased up to an average RE value of 92 ± 5% (corresponding to EC=20.5 ± 1.1 g C m^{-3} h^{-1}) in days 15-36 (Fig. 2). The styrene mineralization was confirmed by the concomitant production of CO_2. The EBRT was decreased from 30 s to 20 s by day 37, which produced a deterioration of the removal performance, an average RE value of 66% (EC < 23 g C m^{-3} h^{-1}) being recorded in days 42-47. A further decrease of the EBRT to 15 s by day 48 led to an average RE value of 41 ± 7% (corresponding to EC=17.9 ± 3.1 g C m^{-3} h^{-1}) in days 50-60. At day 61, although the inlet styrene concentration was decreased from 184 mg C m^{-3} to 92 mg C m^{-3} (EBRT=15 s), an average RE value of 42 ± 10% (corresponding to EC=9.4 ± 2.3 g C m^{-3} h^{-1}) in days 63-67 was still maintained. An increase of the styrene inlet concentration to 323 mg C m^{-3} led to unstable and poor removal performance characterized by RE values between 18% and 42% in days 68-70. Finally, styrene inlet concentration was decreased to 55 mg C m^{-3} (IL=13 g C m^{-3} h^{-1}, EBRT=15 s), obtaining an average RE of 64% (EC= 7.9 ± 0.9 g C m^{-3} h^{-1}). This result was in agreement with previous studies concluding that EBRTs below 30 s led to poor styrene removal performance in conventional BTFs (RE<65%) regardless of the inlet concentration [1,4]. The pressure drop measured throughout the experimental time was below 0.5 mm H_2O m_{bed}^{-1}. TOC measurements in the aqueous phase of the holding tank ranged between 190 and 880 mg C L^{-1}, indicating that the styrene removed each weekly through water renewal represented less than 3% of the total amount of styrene supplied in such period of time. Thus, the styrene removed through aqueous phase renewal was considered as negligible for the EC and RE determination. Table 2 presents a summary of the control BTF performance in terms of elimination capacity and CO_2 production in the experimental phases B and C (the startup period was not included). It was observed 73% and 38% of the C-styrene removed was mineralized in phases B and C, respectively, while the carbon purged through water renewal accounted for 1.3% and 2.5% of the total carbon entering the control BTF in phases B and C, respectively.

<Figure 2>

<Table 2>

Most studies dealing with styrene removal in BTFs have reported REs higher than 80% when EBRTs ≥ 30 s were set [1,4,11,19–22]. In some cases, EBRTs as long as 120 s were required to achieve such a high styrene removal performance [19,20,22]. However, the few studies exploring the styrene removal at EBRTs < 30 s and inlet styrene concentrations ≥ 100 mg C m^{-3} have consistently reported a poor removal performance (e.g. RE<60%) [1,20,21]. As far as the authors know, the only study achieving styrene

RE close to 100% in a BTF operated at EBRT of 20 s was reported by Rene et al. [11] by using inlet styrene concentrations below 300 mg m^{-3} (277 mg C m^{-3}). In this study, the increase in the inlet styrene concentration up to 2100 mg m^{-3} (1936 mg C m^{-3}) progressively hindered the RE up to a value of 53% at an inlet concentration of 1100 mg m^{-3} (1014 mg C m^{-3}).

At this point it is important to stress that biological air treatment technologies are nowadays challenged by industrial end-users to improve the economic feasibility in terms of investment costs [23]. Thus, although an EBRT of 30 s is one of the shortest gas residence times yielding high and stable styrene REs in BTFs further optimization in terms of EBRT is still necessary to reduce the size of the BTF and, consequently, reduce the investment cost of the treatment technology [24].

3.2. Removal performance of the TPPB-BTF

Unlike the control BTF, a significant biomass attachment on the packing material in the TPPB-BTF was observed only after 15 days of operation. The intermittent liquid recycling set at day 6 promoted the biomass attachment on the packed bed, which was related to an increasing removal performance. From days 20 to 36, the TPPB-BTF supported an average RE of 92±4% (corresponding to EC=19.0 ± 1.0 g C m^{-3} h^{-1}) (Fig. 3). The styrene mineralization was confirmed by the concomitant production of CO_2. Therefore, although the TPPB-BTF required approximately 10 days more than the control BTF to achieve RE>80%, both bioreactors supported a similar and stable removal performance when operated at EBRT of 30 s and styrene inlet concentration of 184 mg C m^{-3}.

<Figure 3>

EBRT reduction from 30 s to 20 s by day 37 produced a slight drop of the removal performance for two days (RE of ~80%). Thereafter, the removal performance was recovered and the TPPB-BTF supported an average RE of 91±2% (corresponding to EC=27.1 ± 1.7 g C m^{-3} h^{-1}) in days 38-47. At day 48, a further decrease of the EBRT to 15 s hindered the removal performance, resulting in RE of 71±5% (corresponding to EC=30.8 ± 2.6 g C m^{-3} h^{-1}) in days 50-60. It is worth noting that the control BTF supported a RE of 41±7% under the same operating conditions, which demonstrated the superior performance of the TTPB-BTF. A decrease in the inlet styrene concentration at day 61, from 184 mg m^{-3} to 92 mg C m^{-3} (while maintaining an EBRT=15 s), resulted in a significant increase of the removal performance. An average RE of 84±3% (corresponding to EC=19.1 ± 1.1 g C m^{-3} h^{-1}) was recorded in days 62-67. This styrene RE constitutes the best removal performance for a BTF operated at an EBRT of 15 s, which is one of the shortest gas residence times so far reported for styrene abatement. Then, the styrene inlet concentration was increased to 323 mg C m^{-3} by day 68, leading to a drop in the styrene abatement performance up to a RE of 57±4% (corresponding to EC=43.2 ± 1.5 g C m^{-3} h^{-1}). At day 71, while maintaining an EBRT = 15 s, the inlet concentration was decreased from 323 to 55 mg C m^{-3}, resulting in a RE increase of up to 89% (EC= 11.7 g C m^{-3} h^{-1}).

The presence of silicone oil did not increase the pressure drop in the TPPB-BTF, which was below 0.5 mm H_2O m_{bed}^{-1} throughout the whole experimental time. TOC measurements in the aqueous phase of the holding tank ranged between 350 and 2765 mg C L^{-1}. This amount of styrene weekly removed through water renewal represented less than 4% of the total styrene supplied in such period of time and was therefore considered as negligible for EC and RE determination. Table 3 presents a summary of the TPPB-BTF performance in terms of elimination capacity and CO_2 production in the experimental phases B and C (the startup period was not included). It was observed that ~58% of the C-styrene removed was mineralized in phases B and C, while the carbon purged through water renewal accounted for 3.9% and 3.2% of the total carbon entering the TPPB-BTF in phases B and C, respectively.

<Table 3>

Overall, the TPPB-BTF supported a higher removal performance compared with the control BTF in all the operating conditions tested. Although biomass attachment on the packed bed of the TPPB-BTF took approximately 10 days more than in the control BTF, once the biofilm was developed, the removal in the TPPB-BTF was stable and robust over the experimental time. Recent studies also investigated the performance of TPPB-BTFs using silicone oil as the NAP for the removal of styrene [11,19]. These studies confirmed that the addition of silicone oil at 1.6-8.0 % (relative to the packed bed volume) drastically improved the styrene removal performance. Rene et al. [11] investigated the styrene removal in a BTF with inlet concentrations of 0.1-24 g m^{-3} (0.092-22 g C m^{-3}) and EBRTs of 20-91 s. These authors reported a RE of 100% at EBRT of 20 s when the styrene inlet concentration was $\leq$ 2 g m^{-3} (1.8 g C m^{-3}). Moreover, styrene inlet concentrations in the range of 2-24 g m^{-3} (1.8-22 g C m^{-3}) are far higher than those typically found in real-case emissions. VOC recovery technologies rather than destructive processes are actually recommended for concentrations higher than 5 g m^{-3} [24]. Zamir et al. [19] studied styrene removal in the presence of silicone oil at inlet concentrations of 0.8-3.3 g m^{-3} (0.7-3 g C m^{-3}) and EBRTs of 1 and 2 min. They achieved REs $\geq$ 90% at EBRT of 2 min, regardless of the styrene concentration. Although these authors also tested styrene concentrations higher than that found in real-case emissions, they demonstrated the superior removal performance of TPPB-BTFs relative to controls without silicone oil.

One of the main differences among previous reports on styrene abatement in TPPB-BTFs and the present study was the inoculation protocol. The inoculation procedures previously reported, considered the addition of biomass and silicone oil as separated stages [11,19]. In the present study, the TPPB-BTF was inoculated with hydrophobic biomass attached to silicone oil following the protocol described by Muñoz et al. [17]. For 60 days, styrene-degrading microorganisms able to accumulate into silicone oil were enriched from an activated sludge by periodical removal of aqueous phase during acclimation. Thus, when the biomass-loaded silicone oil was added, the bioreactor was inoculated. Hydrophobic biomass attached to silicone oil was expected to improve the TPPB performance by allowing the direct pollutant uptake from silicone oil, avoiding the additional NAP-to-biomass mass transfer step as previously reported [17,25,26]. Furthermore, the microbial communities able to grow immersed in silicone oil must also exhibit a higher tolerance to styrene due to the process selection used for inoculation. The results herein obtained indeed showed that this inoculation strategy allowed a high styrene removal performance even at an EBRT as low as 15 s.

Figure 4 depicts the relationship between EC and IL at EBRT of 15 s. The maximum ECs obtained were 28 ± 4 g C m^{-3} h^{-1} (IL of 74 g C m^{-3} h^{-1}) for the control BTF and 43 ± 2 g C m^{-3} h^{-1} (IL of 77 g C m^{-3} h^{-1}) for the TPPB-BTF. The critical IL for control BTF at this low EBRT was ~9 g C m^{-3} h^{-1} while for TPPB-BTF was ~23 g C m^{-3} h^{-1}. To the best of our knowledge, only Sempere et al. [1] reported styrene removal data in a BTF operated at an EBRT of 15 s. These authors observed REs between 20-60% using an EBRT of 15 s at inlet loads around 20-100 g C m^{-3} h^{-1}, obtaining a maximum EC of ~30 g C m^{-3} h^{-1}. Therefore, the TPPB-BTF here proposed supporting REs of up to 90% at similar inlet loads and EBRT of 15 s demonstrates a superior styrene removal performance relative to conventional BTFs.

<Figure 4>

3.3. Removal performance of the TPPB-BTF under transient conditions

Industrial emissions are usually characterized by variable concentrations related to the manufacturing shifts. On days 76 and 77, the effect of this variable inlet concentration on the transient response of the TPPB-BTF was evaluated. Two different concentration patterns were applied at EBRT of 15 s, in order to simulate typical shock loadings found in the industry. The first pattern consisted of 4 cycles of alternating inlet concentration of 92 mg C m^{-3} (IL= 22 g C m^{-3} h^{-1}) and peaks of 645 mg C m^{-3} (IL= 155 g C m^{-3} h^{-1}) of 2 hours duration each one. As shown in Fig. 5a, for an inlet concentration of 92 mg C m^{-3} a RE of ~75% was obtained, while at an inlet concentration of 645 mg C m^{-3} the RE drastically dropped to ~20%.

The second transient loading pattern consisted of 3 cycles of inlet concentration fluctuations of 92, 415, 184, 553 and 323 mg C m^{-3} (ILs= 22, 100, 44,133 and 77 g C m^{-3} h^{-1}, respectively). As shown in Fig. 5b, REs ranging from ~80% to ~55% were obtained for inlet concentrations between 92 and 323 mg C m^{-3}, respectively. At higher styrene inlet concentrations (e.g. 415 and 553 mg C m^{-3}), the REs dropped up to 40%.

<Figure 5>

On day 78, the continuous styrene feeding was restored at an IL of 34 g C m^{-3} h^{-1} (EBRT= 20 s) in order to evaluate the resilience of the TPPB-BTF after the transient conditions. It was observed that a stable RE of ~85% (EC= 30 g C m^{-3} h^{-1}) was obtained one day just after the operation disturbances were set and it was maintained during more than 2 weeks (until day 97). This removal performance was similar to that obtained in days 38-47 with the same IL and EBRT. Hence, the TPPB-BTF was able to recover from styrene shock loadings, demonstrating the robustness of the TPPB-BTF over transient operating conditions.

3.4. Potential of TPPB-BTFs for full-scale applications

The development of TPPBs for VOC removal with potential for full-scale applications has been challenged by three main constraints: (i) implementation in bioreactor configurations applicable at industrial scale, (ii) the cost of the NAP, and (iii) potential losses of NAP during the aqueous phase renewal [12,27]. Regarding the bioreactor configuration, several studies already demonstrated that TPPBs can be successfully implemented in configurations currently used at industrial scale such as BTFs and biofilters [12,28]. In the present study it was also demonstrated that the use of polypropylene rings, a packing material widely used in industrial BTFs, allowed the operation of the TPPB-BTF with pressure drops as low as 0.3 mm H_2O m_{bed}^{-1} throughout the experimental time. Therefore, even industrial BTFs already set in industrial facilities might be operated as TPPB-BTFs.

Regarding the cost of the NAP, Daugulis et al. [27] pointed out the high cost of silicone oil as its main disadvantage towards TPPB implementation at full-scale. However, these authors considered the cost of analytical-grade silicone oil, which is 40 times more expensive than that of technical-grade silicone oil (230 € L^{-1} *vs* 5.75 € L^{-1}, respectively; 2016 prices from Sigma-Aldrich and Univar-Iberia, Spain). The present study, together with other recent experimental studies, demonstrated that the addition of analytical-grade silicone oil improves both the styrene mass transfer and its biodegradation in BTFs compared with controls without NAP [10,19]. This experimental evidence on the efficacy of low-cost silicone oil to enhance the performance of BTFs certainly encourages the implementation of TPPBs for VOC removal. Considering the NAP percentage of 5%

(relative to the packed bed) used in the present study, an additional investment cost of ~288 € per m^3 of reactor is required for TPPB-BTF implementation relative to a "conventional" BTF. This difference seems to be affordable considering the process improvement in terms of removal performance, robustness and low EBRT required to achieve REs>80%, which finally allows the design of smaller bioreactors (decreasing the overall investment costs).

Potential losses of NAP during the aqueous phase renewal in the TPPB-BTF is another key aspect to be considered to assess both the economic feasibility and the environmental impact of the treatment technology. Aqueous phase renewal in any BTF is required to provide nutrients and avoid the accumulation of toxic metabolites and ions [29]. However, silicone oil losses must be avoided or minimized during this liquid renovation to avoid significant increases of the operating costs and negative impacts on the environment. In the present study, the silicone oil content in the purged aqueous phase was quantified through SiO_2 measurements (1 g of silicone oil contains ~0.59 g of SiO_2). The SiO_2 concentrations measured in days 35, 42, 49, 61 and 87 were 61, 235, 250, 79 and 173 g m_{water}^{-3}, respectively. Considering an average value of 160 ± 87 gSiO_2 m_{water}^{-3}, the silicone oil density of 0.96 g mL^{-1} and that 3 L of aqueous phase were exchanged each 7 days, then 3.4 ± 1.8 mL of silicone oil were purged every month. This amount of silicone oil represents 0.4% of the initially added silicone oil, showing that only a small fraction of the oil is prone to be purged through aqueous phase renewal as most silicone remains retained within the packed bed. This was particularly evident in the TPPB-BTF herein implemented since the hydrophobic biomass attached to the silicone oil promoted the oil retention on the packing material. This oil retention on the packed bed of a TPPB-BTF was also reported by Zamir et al. [19]. On the other hand, silicone oils of low viscosity (e.g. kinematic viscosity ≤ 200 cSt) are ubiquitous in personal and household care products such as shampoos, hair conditioners and silicone antifoams in detergents [30]. Therefore, high amounts of silicone oils are currently treated in municipal WWTPs. As a matter of fact, more than 95% of silicones are removed in WWTPs [30,31]. The small leak of silicone oil observed during this study indicates that there are no additional concerns during water renewal in usual TPPB-BTF operation for VOC removal.

4. Conclusions

This study confirmed the superior styrene abatement performance of a TPPB-BTF implemented with industrial-grade silicone oil over a conventional BTF without a NAP. Stable removal efficiencies of up to 84-89% were achieved in the TPPB-BTF even at an EBRT as low as 15 s, which constitutes one of the shortest residence times so far reported in the literature for styrene abatement in BTFs. For this EBRT, the critical IL (around 23 g C m^{-3} h^{-1}) increased more than two times the value observed for the conventional BTF. The TPPB-BTF exhibited a high and stable RE after applying styrene shock loadings and transient operating conditions, which demonstrated its resilience and robustness over transitory conditions commonly found in real-case emissions. After 87 days of operation, silicone oil loses through water renewal accounted for 0.4% of the initial volume of NAP added to the TPPB-BTF. This small silicone oil leak did not induced decreases in the styrene removal performance and neither constitutes a critical drawback for the economy and sustainability of the treatment technology.

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References

[1] F. Sempere, V. Martínez-Soria, J. Palau, J.-M. Penya-Roja, P. San-Valero, C. Gabaldón, Effects of nitrogen source and empty bed residence time on the removal of styrene gaseous emissions by biotrickling filtration, Bioprocess Biosyst. Eng. 34 (2011) 859–67. doi:10.1007/s00449-011-0536-9.

[2] R.R. Miller, R. Newhook, A. Poole, Styrene Production, Use, and Human Exposure, Crit. Rev. Toxicol. 24 (1994) 1–10. doi:10.3109/10408449409020137.

[3] E. Dumont, Y. Andrès, Styrene absorption in water/silicone oil mixtures, Chem. Eng. J. 200-202 (2012) 81–90. doi:10.1016/j.cej.2012.06.028.

[4] M.C. Pérez, F.J. Álvarez-Hornos, K. Portune, C. Gabaldón, Abatement of styrene waste gas emission by biofilter and biotrickling filter: comparison of packing materials and inoculation procedures, Appl. Microbiol. Biotechnol. (2014) 19–32. doi:10.1007/s00253-014-5773-9.

[5] K.J. Portune, M.C. P??rez, F.J. ??lvarez-Hornos, C. Gabald??n, Investigating bacterial populations in styrene-degrading biofilters by 16S rDNA tag pyrosequencing, Appl. Microbiol. Biotechnol. 99 (2014) 3–18. doi:10.1007/s00253-014-5868-3.

[6] WHO, World Health Organization - air quality guidelines for Europe, (2000).

[7] S. El Aalam, A. Pauss, J.-M. Lebeault, High efficiency styrene biodegradation in a biphasic organic/water continuous reactor, Appl. Microbiol. Biotechnol. 39 (1993) 696–699. doi:10.1007/BF00164452.

[8] J.M. Estrada, R. Lebrero, G. Quijano, N.J.R. Kraakman, R. Muñoz, Strategies for Odour Control, in: V. Belgiorno, V. Naddeo, T. Zarra (Eds.), Odour Impact Assess. Handb., John Wiley & Sons, Inc., Hoboken, NJ, USA, 2013: pp. 85–124. doi:10.1002/9781118481264.ch4.

[9] E. Dumont, Y. Andrès, P. Le Cloirec, Mass transfer coefficients of styrene into water/silicone oil mixtures: New interpretation using the “equivalent absorption capacity” concept, Chem. Eng. J. 237 (2014) 236–241. doi:10.1016/j.cej.2013.10.021.

[10] P. Parnian, S.M. Zamir, S.A. Shojaosadati, Styrene vapor mass transfer in a biotrickling filter: Effects of silicone oil volume fraction, gas-to-liquid flow ratio, and operating temperature, Chem. Eng. J. 284 (2016) 926–933. doi:10.1016/j.cej.2015.08.148.

[11] E.R. Rene, M. Montes, M.C. Veiga, C. Kennes, Styrene removal from polluted air in one and two-liquid phase biotrickling filter: steady and transient-state performance and pressure drop control., Bioresour. Technol. 102 (2011) 6791–800. doi:10.1016/j.biortech.2011.04.010.

[12] R. Muñoz, A.J. Daugulis, M. Hernández, G. Quijano, Recent advances in two-phase partitioning bioreactors for the treatment of volatile organic compounds, Biotechnol. Adv. 30 (2012) 1707–20. doi:10.1016/j.biotechadv.2012.08.009.

[13] P. Osswald, P. Baveye, J.C. Block, Bacterial influence on partitioning rate during the biodegradation of styrene in a biphasic aqueous-organic system, Biodegradation. 7 (1996) 297–302. doi:10.1007/BF00115743.

[14] C. Kennes, E.R. Rene, M.C. Veiga, Bioprocesses for air pollution control, J. Chem. Technol. Biotechnol. 84 (2009) 1419–1436. doi:10.1002/jctb.2216.

[15] F. Sempere, C. Gabaldón, V. Martínez-Soria, P. Marzal, J.M. Penya-roja, F.J. Alvarez-Hornos, Performance evaluation of a biotrickling filter treating a mixture of oxygenated VOCs during intermittent loading, Chemosphere. 73 (2008) 1533–1539. http://www.sciencedirect.com/science/article/B6V74-4TMRJYH-1/2/f000c5a77b90f8d6d0c18d3e44869acb.

[16] J.S. Devinny, J. Ramesh, A phenomenological review of biofilter models, Chem. Eng. J. 113 (2005) 187–196. doi:10.1016/j.cej.2005.03.005.

[17] R. Muñoz, E.I.H.H. Gan, M. Hernández, G. Quijano, Hexane biodegradation in two-liquid phase bioreactors: High-performance operation based on the use of hydrophobic biomass, Biochem. Eng. J. 70 (2013) 9–16. doi:10.1016/j.bej.2012.09.009.

[18] F. Sempere, V. Martínez-Soria, J.-M. Penya-roja, M. Izquierdo, J. Palau, C. Gabaldón, Comparison between laboratory and pilot biotrickling filtration of air emissions from painting and wood finishing, J. Chem. Technol. Biotechnol. 85 (2010) 364–370. doi:10.1002/jctb.2327.

[19] S.M. Zamir, S. Babatabar, S.A. Shojaosadati, Styrene vapor biodegradation in single- and two-liquid phase biotrickling filters using Ralstonia eutropha, Chem. Eng. J. 268 (2015) 21–27. doi:10.1016/j.cej.2015.01.040.

[20] J.W. Hwang, C.Y. Choi, S. Park, E.Y. Lee, Biodegradation of gaseous styrene by Brevibacillus sp using a novel agitating biotrickling filter, Biotechnol. Lett. 30 (2008) 1207–1212. doi:10.1007/s10529-008-9670-0.

[21] T. Song, C. Yang, G. Zeng, G. Yu, C. Xu, Effect of surfactant on styrene removal from waste gas streams in biotrickling filters, J. Chem. Technol. Biotechnol. 87 (2012) 785–790. doi:10.1002/jctb.3717.

[22] D. Kim, Z. Cal, G.A. Sorial, Evaluation of Trickle-Bed Air Biofilter Performance under Periodic Stressed Operating Conditions as a Function of Styrene Loading, J. Air Waste Manage. Assoc. 55 (2005) 200–209. doi:10.1080/10473289.2005.10464611.

[23] A. Santos, X. Guimerà, A.D. Dorado, X. Gamisans, D. Gabriel, Conversion of chemical scrubbers to biotrickling filters for VOCs and H2S treatment at low contact times., Appl. Microbiol. Biotechnol. 99 (2015) 67–76. doi:10.1007/s00253-014-5796-2.

[24] R. Muñoz, L. Malhautier, J.-L. Fanlo, G. Quijano, Biological technologies for the treatment of atmospheric pollutants, Int. J. Environ. Anal. Chem. 95 (2015) 950–967. doi:10.1080/03067319.2015.1055471.

[25] M. Hernández, G. Quijano, R. Muñoz, Key role of microbial characteristics on the performance of VOC biodegradation in two-liquid phase bioreactors, Environ. Sci. Technol. 46 (2012) 4059–66. doi:10.1021/es204144c.

[26] A.D. Dorado, E. Dumont, R. Muñoz, G. Quijano, A novel mathematical approach for the understanding and optimization of two-phase partitioning bioreactors devoted to air pollution control, Chem. Eng. J. 263 (2015) 239–248. doi:10.1016/j.cej.2014.11.014.

[27] A.J. Daugulis, M.C. Tomei, B. Guieysse, Overcoming substrate inhibition during biological treatment of monoaromatics: recent advances in bioprocess design., Appl. Microbiol. Biotechnol. 90 (2011) 1589–608. doi:10.1007/s00253-011-3229-z.

[28] G. Quijano, M. Hernandez, F. Thalasso, R. Muñoz, S. Villaverde, Two-phase partitioning bioreactors in environmental biotechnology, Appl. Microbiol. Biotechnol. 84 (2009) 829–846. doi:10.1007/s00253-009-2158-6.

[29] H.H.J. Cox, M.A. Deshusses, Biological waste air treatment in biotrickling filters, Curr. Opin. Biotechnol. 9 (1998) 256–262.

[30] R. Watts, S. Kong, C.S. Haling, L. Gearhart, C.L. Frye, B.W. Vigon, Fate and effects of polydimethylsiloxanes on pilot and bench-top activated sludge reactors and anaerobic/aerobic digesters, Water Res. 29 (1995) 2405–2411. doi:10.1016/0043-1354(95)00067-U.

[31] N.J. Fendinger, D.C. McAvoy, W.S. Eckhoff, B.B. Price, Environmental Occurrence of Polydimethylsiloxane, Environ. Sci. Technol. 31 (1997) 1555–1563. doi:10.1021/es9608712.

Figure Captions

Fig. 1. Schematic of the experimental set-up. Continuous and dashed lines represent liquid and gas streams, respectively.

Fig. 2. Time course of (a) styrene IL (□), removal efficiency (◆, secondary axis), and (b) EC (▲), CO_2 production (○, secondary axis) in the control BTF. Vertical gray arrows indicate aqueous phase renewal.

Fig. 3. Time course of (a) styrene IL (□), removal efficiency (◆, secondary axis), and (b) EC (▲), CO_2 production (○, secondary axis) in the TPBB-BTF. Vertical gray arrows indicate aqueous phase renewal.

Fig. 4. Relationship between the styrene EC and IL at EBRT of 15 s, in the control BTF (●) and TPBB-BTF (○).

Fig. 5. Performance of the TPPB-BTF under shock loadings and transient conditions at EBRT of 15 s, where: (a) shock loading pattern set in day 76, and (b) transient emission pattern set in day 77.

Table 1. Operating conditions set in the TPPB-BTF and BTF.

Phase	**Stage**	**Days**	**Styrene inlet concentration ($mg\ m^{-3}$)**	**IL ($g\ m^{-3}\ h^{-1}$)**	**EBRT (s)**	**Liquid recycling**
A	Startup	0-5	200	24	30	Continuous
B	1	6-36	200	24	30	Intermittent: operating for 15 min every 2 h
	2	37-47	200	36	20	
	3	48-60	200	48	15	
C	1	61-67	100	24	15	
	2	68-70	350	84	15	
	3	71-75	60	14	15	

Figure 1.

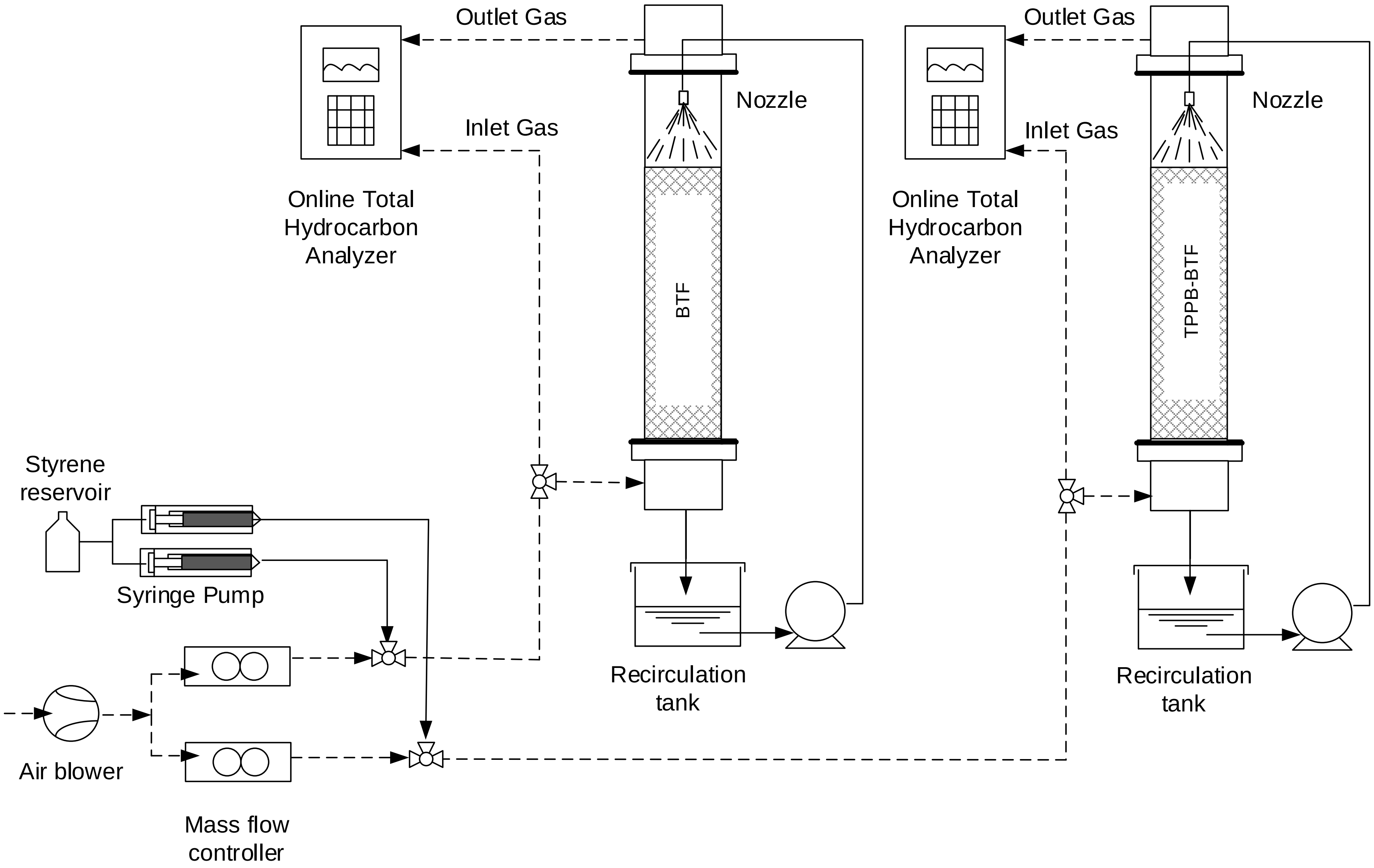

Outlet Gas
Nozzle
Inlet Gas
Online Total Hydrocarbon Analyzer
BTF
Outlet Gas
Nozzle
Inlet Gas
Online Total Hydrocarbon Analyzer
TPPB-BTF
Styrene reservoir
Syringe Pump
Recirculation tank
Recirculation tank
Air blower
Mass flow controller

Figure 2.

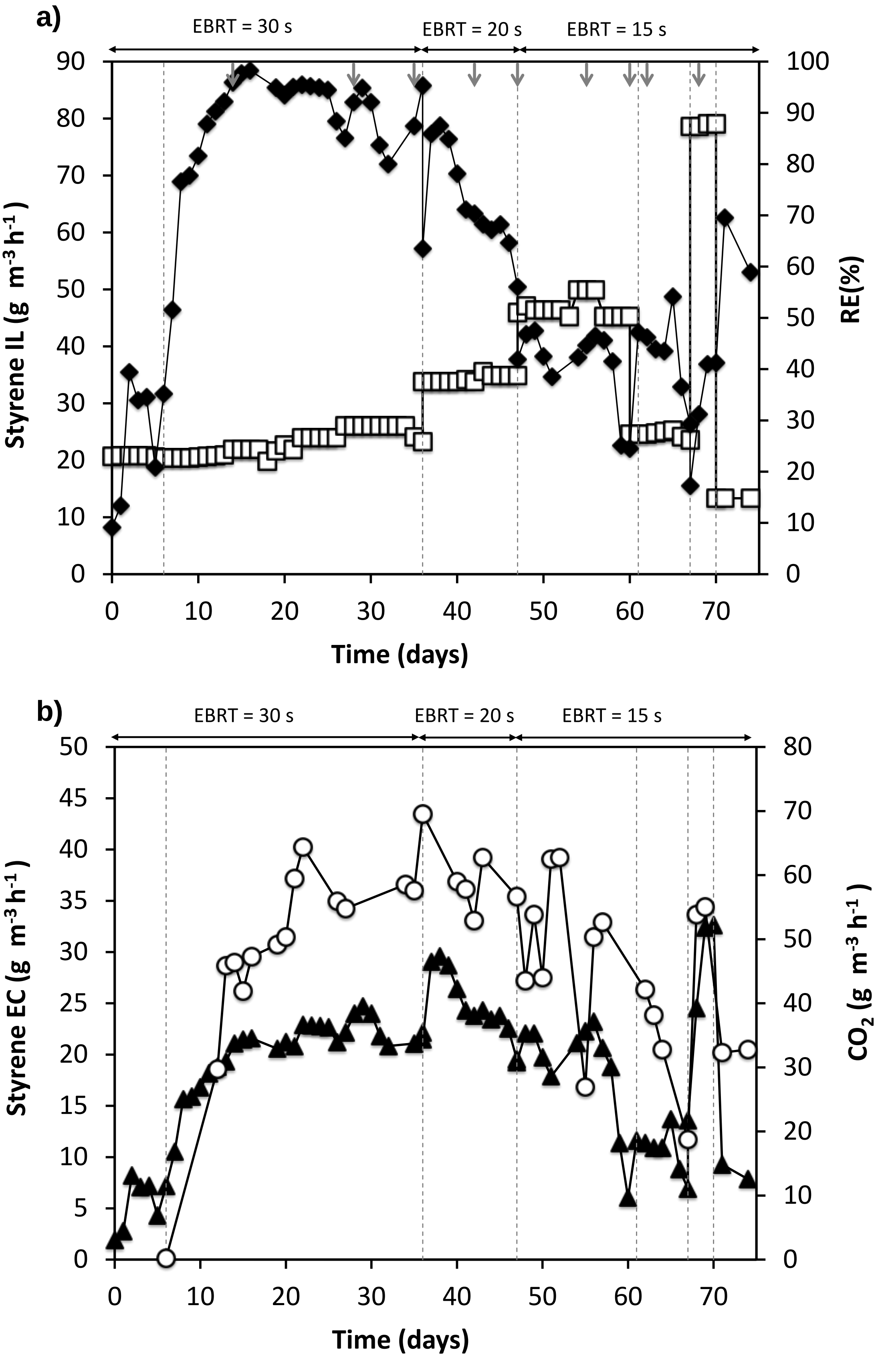

a)
EBRT = 30 s
EBRT = 20 s
EBRT = 15 s
Styrene IL (g m^{-3} h^{-1})
RE(%)
Time (days)
0
10
20
30
40
50
60
70
80
90
100
b)
EBRT = 30 s
EBRT = 20 s
EBRT = 15 s
Styrene EC (g m^{-3} h^{-1})
CO$_2$ (g m^{-3} h^{-1})
Time (days)
0
5
10
15
20
25
30
35
40
45
50
60
70
80

Figure 3.

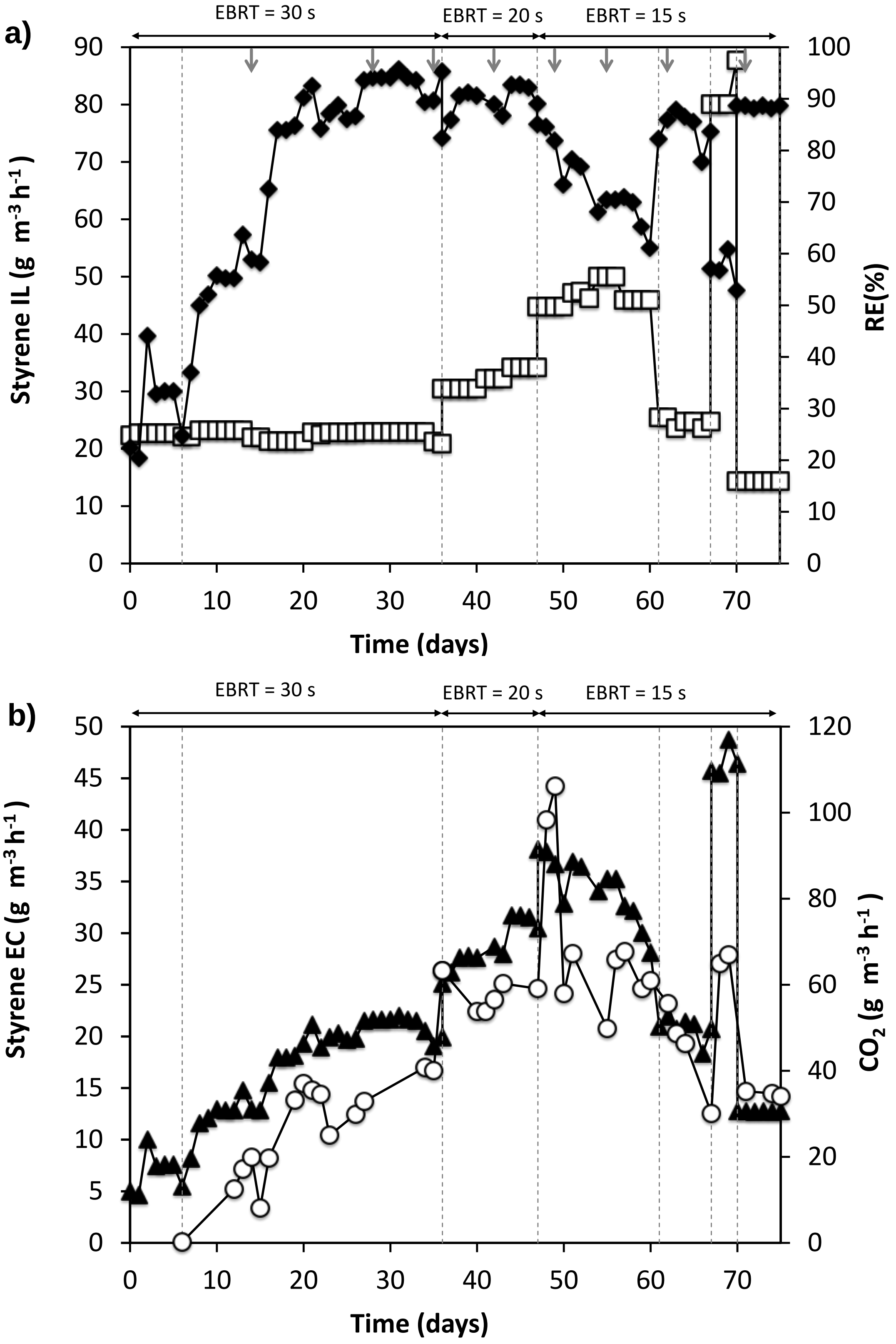

a)
EBRT = 30 s
EBRT = 20 s
EBRT = 15 s
Styrene IL (g m-3 h-1)
RE(%)
Time (days)
0
10
20
30
40
50
60
70
80
90
100
b)
EBRT = 30 s
EBRT = 20 s
EBRT = 15 s
Styrene EC (g m-3 h-1)
CO2 (g m-3 h-1)
Time (days)
0
5
10
15
20
25
30
35
40
45
50
60
80
100
120

Figure 4.

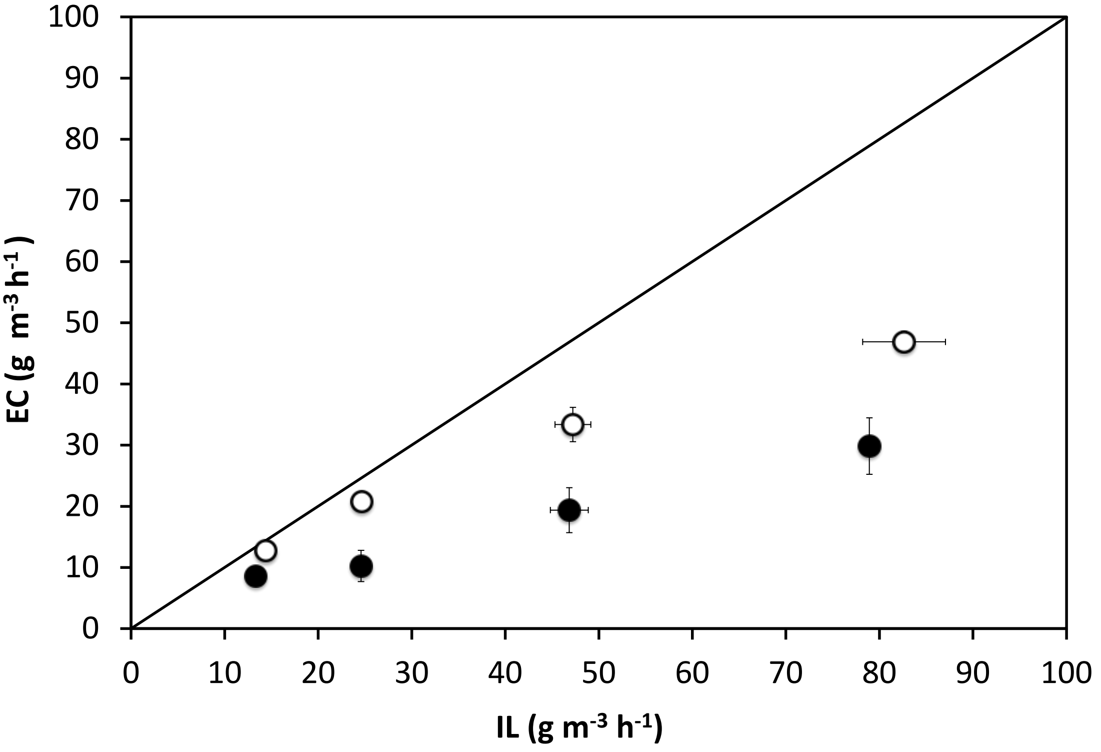

100
90
80
70
60
50
40
30
20
10
0
EC (g m-3 h-1)
0
10
20
30
40
50
60
70
80
90
100
IL (g m-3 h-1)

Figure 5.

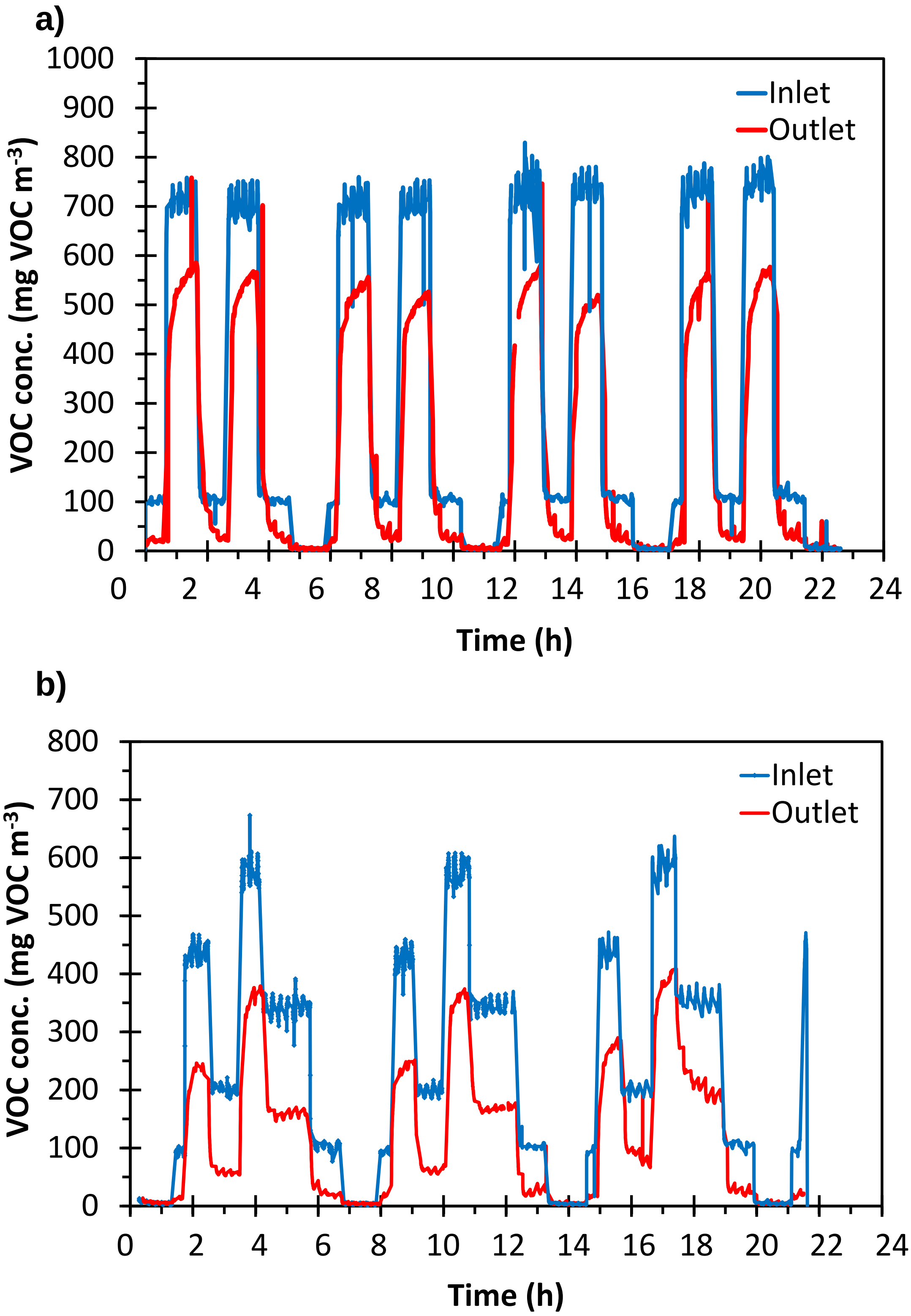
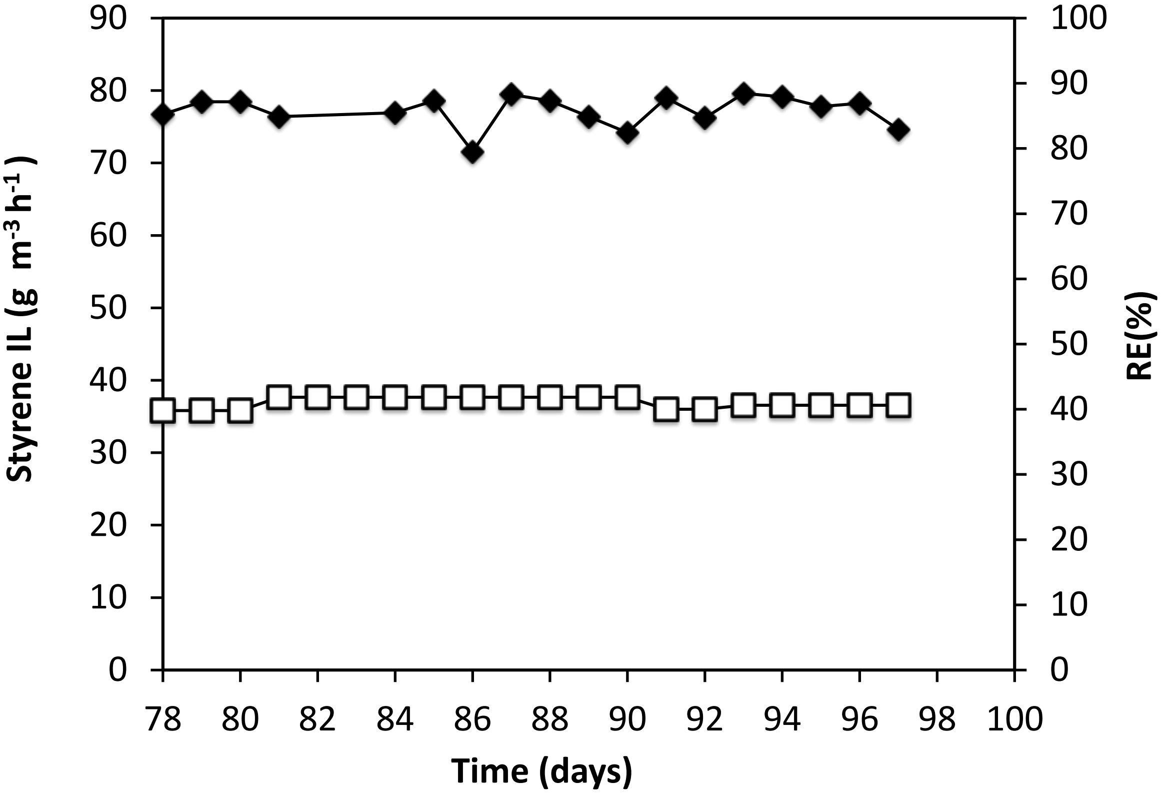

a)
VOC conc. (mg VOC m^{-3})
0
100
200
300
400
500
600
700
800
900
1000
Time (h)
0
2
4
6
8
10
12
14
16
18
20
22
24
Inlet
Outlet
b)
VOC conc. (mg VOC m^{-3})
0
100
200
300
400
500
600
700
800
Time (h)
0
2
4
6
8
10
12
14
16
18
20
22
24
Inlet
Outlet

Figure 6.


Styrene IL (g m^{-3} h^{-1})
RE(%)
Time (days)
0
10
20
30
40
50
60
70
80
90
100
78
80
82
84
86
88
90
92
94
96
98
100