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Comparative Evaluation of a Biotrickling Filter and a Tubular Photobioreactor for the Continuous Abatement of Toluene

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Volatile Organic Compounds (VOCs) are among the gas pollutants with a higher detrimental impact on human health and the environment. The increasing awareness of the population on the importance of air quality and the enforcement of stricter environmental regulations regarding the anthropogenic emissions of these hazardous pollutants have triggered the development of cost-efficient, environmentally friendly off-gas treatment technologies. Biological technologies such as biotrickling filters have been consistently proven as well stablished technologies for the treatment of VOC emissions, although the low solubility of oxygen might limit the aerobic degradation when treating high concentrations of VOCs. In this context, the synergic effects between microalgae and bacteria represent a sustainable platform to promote the simultaneous abatement of VOCs and CO_2 by increasing the dissolved oxygen concentration as a result of the photosynthetic process. In this study, a conventional biotrickling filter (BTF) and an innovative tubular photobioreactor (TPBR) inoculated with a microalgal-bacterial consortium, and interconnected to an external absorption, column were comparatively evaluated for toluene removal. Operating parameters such as the gas residence time (GRT) and the mineral salt medium renewal rate were optimized in order to boost toluene removal. In this sense, both bioreactors were capable of achieving removals > 85 % at a GRT of 45 s and a medium renewal rate of 800 mL d^{-1}. Maximum toluene elimination capacities of ~21 g m^{-3} h^{-1} were recorded in both the BTF and the TPBR. Despite the satisfactory performance of both systems, the photobioreactor presented a competitive advantage due to the capacity of algal biomass to fix the produced CO_2, considerably reducing the emissions of this greenhouse gas, while increasing the concentration of dissolved oxygen in the cultivation broth up to 7.7 mg O_2 L^{-1}.

1. Introduction

Toluene is a volatile aromatic hydrocarbon commonly used as solvent in many industrial sectors such as petrochemistry, pulp and paper or paint and dye (Akmirza et al., 2016). It is included among the priority gaseous organic pollutants, and its emission pose a major challenge due to the detrimental effects on the environment and human health (Mudliar et al., 2010). The toxicity and carcinogenicity of toluene has triggered the enforcement of stringent regulations and, consequently, boosted the necessity of implementing cost effective and environmentally friendly treatment technologies (Wang et al., 2013). The application of physical-chemical processes for the abatement of toluene-laden waste gas streams (such as absorption, adsorption or incineration) is usually inconvenient due to the high flow rates and relatively low volatile organic compounds (VOCs) concentrations that characterize these emissions (Lebrero et al., 2016). Alternatively, biological processes for the aerobic biodegradation of toluene have demonstrated high removal efficiencies at lower operating costs and reduced environmental impacts (Lebrero et al., 2010).
Among biotechnologies, biotrickling filters (BTFs) exhibit advantages over their biological competitors, such as a better process stability and pH control (and thus a more effective treatment of acid-producing pollutants), lower pressure drops and lower footprints thanks to the continuous trickling of water and nutrients (Lebrero et

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al., 2012; Mudliar et al., 2010). However, the treatment of high concentrations of VOCs might cause a limitation of the oxygen available for the aerobic degradation due to its low water-solubility (Mudliar et al. 2010). In this context, the synergic effects between microalgae and bacteria represents an efficient platform to support the simultaneous abatement of CO_2 and VOCs. In this process, heterotrophic bacteria oxidize organic compounds utilizing the additional O_2 produced by the photosynthetic activity of microalgae in the presence of light (Lebrero et al., 2016). Furthermore, the fixation of carbon dioxide results in biomass build-up (photosynthetic fixation of 1 kg of CO_2 may support the production of 0.54 kg of algal biomass, Toledo-Cervantes et al., 2017), which can be further valorized into added-value products. Nevertheless, limited studies have been carried out to analyse the performance of algal-based photobioreactors for the abatement of toluene from a waste gas stream. This work systematically compared the continuous toluene degradation in a conventional BTF and an innovative closed tubular photobioreactor (TPBR) inoculated with an algal-bacterial consortium and interconnected to an absorption column.

2. Materials and Methods

2.1 Inoculum and mineral medium preparation

The BTF was inoculated with 0.5 L of activated sludge from Valladolid wastewater treatment plant (Spain) at a final concentration of total suspended solids (TSS) of 5.2 g L^{-1}, while the TPBR was inoculated with 0.5 L of the same sludge and 1.2 L of a microalgae culture (final TSS = 5.9 g L^{-1}) retrieved from a laboratory scale photobioreactor treating biogas. The mineral salt medium (MSM) used in both bioreactors was composed of (g L^{-1}): Na_2HPO_4 (2.44); KH_2PO_4 (1.52); NH_4SO_4 (1); $MgSO_4 \cdot 7H_2O$ (0.2) and $CaCl_2 \cdot 2H_2O$ (0.05). Trace elements were supplied by adding 10 mL L^{-1} of SL-4 stock solution containing (g L^{-1}): EDTA (0.5); $FeSO_4 \cdot 7H_2O$ (0.2) and 100 mL L^{-1} of SL-6 stock solution (g L^{-1}): $ZnSO_4 \cdot 7H_2O$ (0.1); $MnCl_2 \cdot 4H_2O$ (0.03); H_3BO_3 (0.3); $CoCl_2$ (0.2); $CuCl_2 \cdot 2H_2O$ (0.01); $NiCl_2 \cdot 6H_2O$ (0.02); $Na_2MoO_4 \cdot 2H_2O$ (0.03). Toluene was purchased from PANREAC (Barcelona, Spain) with a purity of 99.8%.

2.2 Experimental and analytical procedure

The contaminated stream was obtained by direct injection of liquid toluene into an ambient air stream by means of a liquid syringe pump (Fusion 100, Chemyx Inc., USA). The mixture was allowed to homogenize in a mixing chamber prior feeding both reactors (Figure 1).

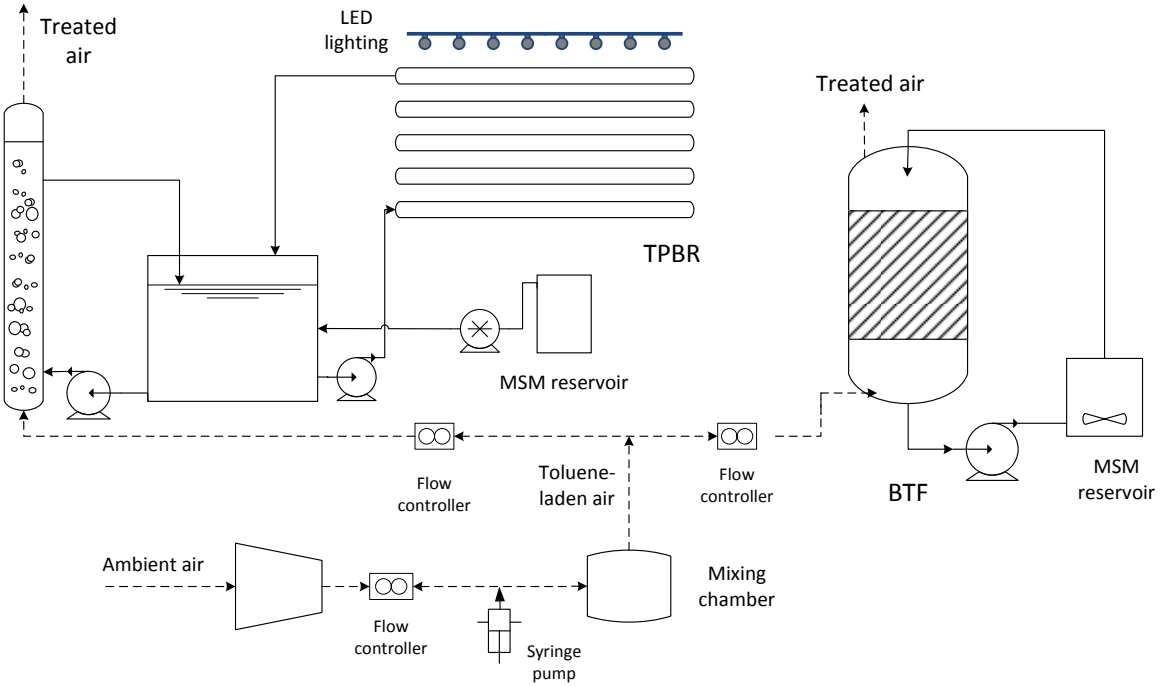

Figure 1: Schematic representation of the experimental setup

The BTF consisted of a cylindrical PVC jacketed column packed with Kaldnes rings, with a working volume of 4 L. The MSM was stored in an external 1.2 L tank under mechanical agitation, and continuously recycled through the packed bed at a trickling liquid velocity (TLV) of 2 m h^{-1}. The toluene-laden stream was supplied

from the bottom of the column. The TPBR had a total working volume of 45.6 L, and was composed of 12 tubes of 6 cm inner diameter and 94 cm length. The photobioreactor was interconnected to a mixing chamber of 60 L volume and an absorption column (AC) of 2 m height, with a working volume of 3.5 L (Figure 1).
The cultivation broth was continuously recirculated from the mixing chamber to the bottom of the AC, and pumped through the TPBR at a linear velocity of 0.53 m s^{-1}. The synthetic contaminated gas stream was supplied via a metallic diffuser located at the bottom of the AC co-currently with the cultivation broth recirculated from the mixing chamber. The liquid to biogas flowrate ratio (L/G) was always maintained at 0.5. Two sets of high intensity LED PCBs (printed circuit boards) were placed at both sides of the photobioreactor at light:dark cycles of 12:12 h of the PAR (photosynthetically active radiation).
The system was operated for ~70 days in order to determine the optimum operating parameters that maximize toluene removal efficiency (Table 1). The gas residence time (GRT) in the BTF and the AC was initially fixed at 2 min (stage I), and subsequently decreased to 1 and 0.75 min in stages II and III-IV, respectively. During stage I, 200 mL of the cultivation broth of the TPBR and of the recycling media in the BTF were daily exchanged by fresh MSM, increasing this MSM renewal rate to 400 (stages II-III), 800 mL d^{-1} (stage IV), respectively. Finally, the toluene inlet concentration was initially set at 0.15 g m^{-3}, doubling this value during the last stage.

Table 1: Operating parameters of the (a) TPBR and (b) BTF during the six operational stages. Cin, tol: inlet toluene concentration; Qg: gas flowrate; IL: toluene inlet load

Stage (days)	$C_{in,tol}$ [g m^{-3}]	Q_g [ml min^{-1}]	GRT [min]	L/G ratio	IL [g m^{-3} h^{-1}]	MSM renewal rate [ml d^{-1}]
I (0-13)	0.15	1100	2	0.5	4.95	200
II (14-37)	0.15	2200	1	0.5	9.9	400
III (38-58)	0.15	2933	0.75	0.5	13.2	400
IV (58-69)	0.3	2933	0.75	0.5	26.4	800

Stage (days)	$C_{in,tol}$ [g m^{-3}]	Qg [mL min^{-1}]	GRT [min]	TLV [m h^{-1}]	IL [g m^{-3} h^{-1}]	MSM renewal rate [mL d^{-1}]
I (0-13)	0.15	2000	2	2	4.5	200
II (14-37)	0.15	4000	1	2	9	400
III (38-58)	0.15	5333	0.75	2	12	400
IV (58-69)	0.3	5333	0.75	2	24	800

Toluene, CO_2, N_2 and O_2 concentrations in the inlet and outlet gas phase of both bioreactors were daily analysed by gas chromatography. Inlet and outlet toluene concentrations in the gas phase were daily analyzed in a Bruker 3900 gas chromatograph (Palo Alto. USA) equipped with a flame ionization detector and a Supelco Wax (15 m × 0.25 mm × 0.25 µm) capillary column. Oven temperature was initially maintained at 50 °C for 1 min, increased at 50 °C min^{-1} up to 70 °C and then at 65 °C min^{-1} to a final temperature of 140 °C. CO_2, N_2 and O_2 concentrations in the gas phase were determined in a Bruker 430 gas chromatograph (Palo Alto, USA) coupled with a thermal conductivity detector and equipped with a CP-Molsieve5A (15 m × 0.53 m × 15 m) and a P-PoraBOND Q (25 m × 0.53 m × 10 m) columns. The oven, injector and detector temperatures were maintained at 40, 150 and 175 °C, respectively. Helium was used as the carrier gas at 13.7 mL min^{-1}. All the injections were carried out with a 100 µl gas-tight glass syringe (Hamilton, USA).
Liquid samples from the BTF leachate and the TPBR mixing chamber were daily taken for pH and dissolved oxygen (DO) analysis, while total organic carbon (TOC), inorganic carbon (IC), total nitrogen (TN) and TSS concentration were determined three times per week. DO concentration in the culture broth of the TPBR was daily monitored by an OXI 330i oximeter (WTW, Germany). The pH of the liquid samples was daily determined by a pH meter Crison 50 12T (Crison Instruments, Spain). Biomass concentration was measured as TSS according to Standard Methods (American Water 167 Works Association, 2012). Samples for the determination of TOC and TN concentrations were filtered through 0.22 µm filters (Merck Millipore. USA) prior to analysis in a TOC-VCSH analyzer (Shimadzu, Japan) coupled with a chemiluminescense detection TN module (TNM-1) (Shimadzu, Japan).

3. Results and Discussion

3.1 Toluene removal performance in the BTF

Following BTF inoculation, the toluene removal performance progressively increased, reaching 92 % by day 2 (Figure 2a).

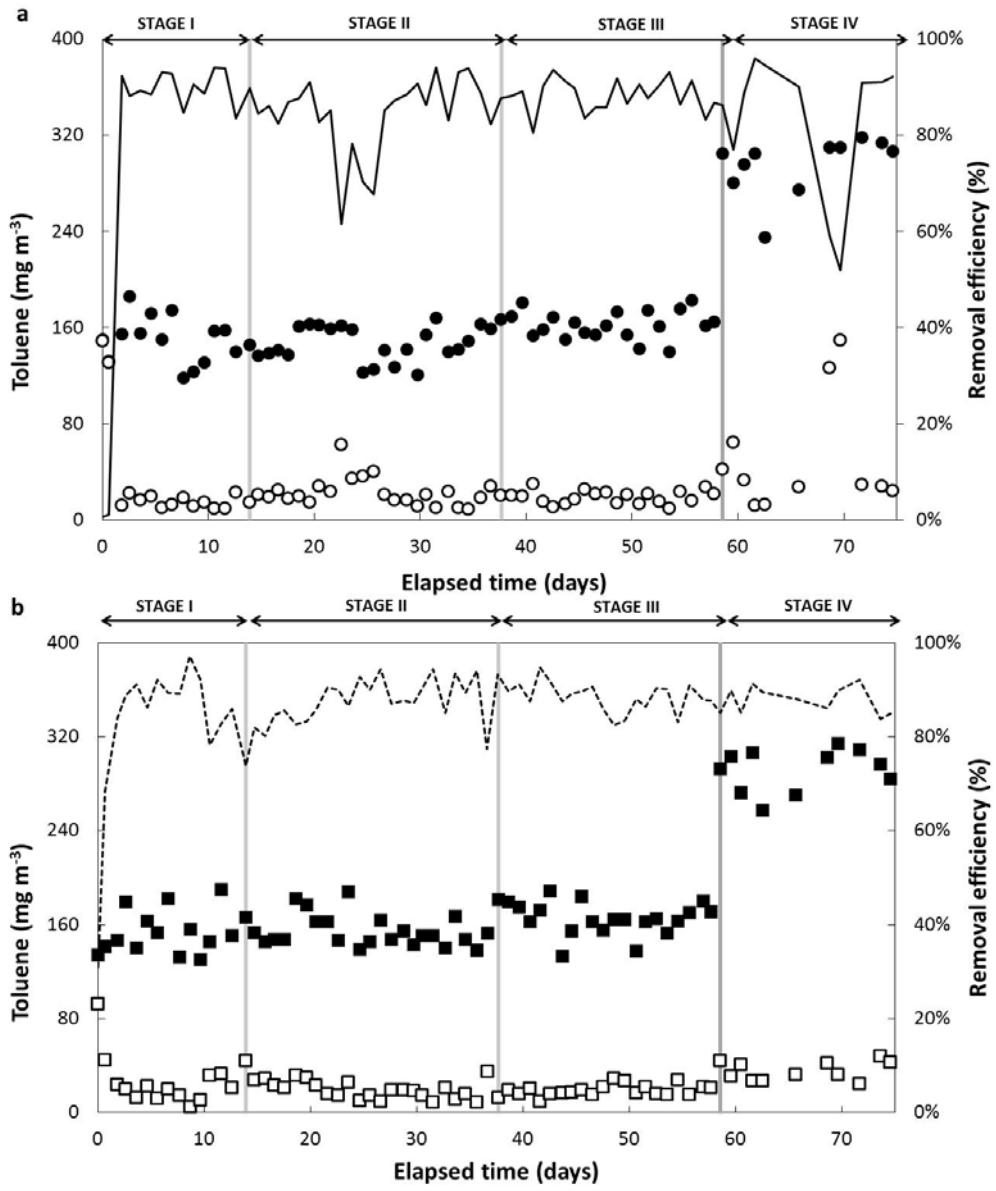

Figure 2: Time course of the inlet (dark symbols) and outlet (white symbols) toluene concentration and toluene removal efficiency (continuous line) in (a) BTF and (b) TPBR. Vertical lines represent the different operating stages as indicated in the upper part of the graphs.

During this first stage, a RE of 90 ± 3 % was maintained, corresponding to an elimination capacity (EC) of 3.5 ± 1.6 g m^{-3} h^{-1}. A slight decrease in the pH was recorded, with a final value of 6.55 by day 13. An average CO_2 production of 10.6 ± 3.9 g m^{-3} h^{-1} was observed, thus resulting in a toluene mineralization of ~71 %. By day 14, the GRT was reduced from 2 to 1 minute, thus increasing the inlet load to ~ 9 g m^{-3} h^{-1}. In order to avoid the accumulation of any possible inhibitory intermediates from the biodegradation process (as previously observed during the aerobic biodegradation of BTEX, Trigueros et al., 2010), the MSM renewal rate was also doubled to 400 mL d^{-1}. A highly fluctuating behavior was observed during stage II, with a sharp decrease in the toluene abatement performance recorded by day 23. Nevertheless, the system was able to recover the

preceding removals, supporting an average RE of 84 ± 8 % and an EC of 7.5 ± 1.0 g m^{-3} h^{-1}. A further decrease in the GRT to 45 s in stage III did not affect the BTF removal capacity, sustaining a RE = 88 ± 3 % and a slightly higher EC of 11.5 ± 1.0 g m^{-3} h^{-1} during this stage. It is important to notice that the pH steadily decreased during stages II and III, reaching values of ~5.5 by the end of this last stage. Moreover, the CO_2 production significantly increased, exceeding the theoretical maximum CO_2 production. Thus, mineralization ratios > 100 % were achieved, probably due to endogenous respiration of the microbial community. By day 58, the potential of the BTF to treat a higher inlet load was tested by doubling the inlet toluene concentration fed to the BTF (at a GRT of 45 s). The MSM renewal rate was also doubled in order to avoid biological inhibition resulting from metabolites accumulation. No alteration of the RE was recorded following the inlet load increase, reaching values up to 96 % by day 62 of operation. A sudden drop in the performance was observed by days 69-70, as a result of a clogging problem in the liquid recycling line. After pipes cleaning, the system rapidly recovered prior performance, and maximum ECs of ~20.5 g m^{-3} h^{-1} were obtained during stage IV. Despite the increase in the MSM renewed, the pH continued to decrease down to values of 3.7-4 by the end of this stage.

3.2 Toluene removal performance in the TPBR

After inoculating the photobioreactor with the algal-bacterial consortia, toluene RE steadily increased, reaching a RE of 89 % by day 2.6 (Figure 2b). A slightly fluctuating behavior was observed during this first stage, with average removals of 88 ± 5 %, corresponding to an EC = 3.8 ± 0.9 g $m^{-3}h^{-1}$. During this stage, the high photosynthetic activity was confirmed by the negative CO_2 production recorded (with outlet CO_2 concentrations below the inlet values) and the high dissolved oxygen concentration in the liquid broth (~7.7 mgO_2 L^{-1}). By day 14 the toluene inlet load was double by reducing the GRT, which resulted in an increase in the toluene EC up to 8.1 ± 0.8 g m^{-3} h^{-1}, corresponding to removals of 87 ± 5 %. The higher carbon load led to an increase in the production of CO_2 and a decrease in the DO concentration to 7.2 mg O_2 L^{-1} due to bacterial activity. Nevertheless, mineralization ratios close to 50 % were obtained due to CO_2 fixation by algal biomass. Similar REs of 89 ± 3 % (with an average EC of 12.8 ± 3.1 g m^{-3} h^{-1}) and mineralization ratios of 42 % were recorded in stage III at a GRT of 45 s. Finally, in stage IV, the system demonstrated its capacity to cope with higher toluene inlet concentrations, maintaining previous removals and reaching maximum ECs = 20.9 ± 1.5 g m^{-3} h^{-1}. It is worth noting that algal biomass increased in this last stage from 0.17 g L^{-1} at the beginning of this stage to 0.27 g L^{-1} by day 74. Thus, the fixation of CO_2 resulted in a final algal biomass productivity of 656 mg d^{-1}. This higher concentration resulted in a reduction of the final CO_2 production, with outlet CO_2 concentrations lower than the inlet values (and therefore negative mineralization ratios were recorded in stage IV). Besides, a slight increase in the DO to 7.4 mg O_2 L^{-1} was also observed. Surprisingly, the photosynthetic activity did not seem to be affected by the low pH recorded throughout the experimentation (decreasing from the initial value of ~ 7 to 5.4 by the end of the operating period).

4. Conclusions

A conventional biotrickling filter and an innovative closed tubular photobioreactor interconnected to an absorption column and inoculated with an algal-bacterial consortium were tested for the abatement of a waste gas stream contaminated with toluene. Both bioreactors demonstrated an efficient toluene removal efficiency > 85 % at gas residence times in the packed bed and the absorption column as low as 45 s. A mineral medium renewal of 800 mL min^{-1} was set at the highest inlet loads treated (~23.5 g m^{-3} h^{-1}) in order to avoid the accumulation of possible inhibitory intermediates. Under these conditions, maximum elimination capacities of 21 g m^{-3} h^{-1} were achieved in both bioreactors. However, the TPBR presented a competitive advantage over its biological counterpart since the photosynthetic activity of the algal biomass resulted in an increase in the dissolved oxygen concentration (reaching values of 7.7 mg O_2 L^{-1}) together with a reduction of the CO_2 emitted in the treated gas stream. Thus, the results obtained in the present study confirmed the suitability of this innovative TPBR set up to efficiently treat toluene emissions while reducing the carbon footprint of the conventional biological technologies.

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