Efficient removal of siloxanes and VOCs from sewage biogas by an anoxic biotrickling filter supplemented with activated carbon

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ABSTRACT

The removal of siloxanes (D4 and D5) and volatile organic contaminants (hexane, toluene and limonene) typically found in sewage biogas was investigated in a lab-scale biotrickling filter (BTF) packed with lava rock under anoxic conditions. Complete removal efficiencies for toluene and limonene were recorded at all empty bed residence time (EBRT) tested. The influence of EBRT was remarkable on the abatement of D5, whose removal decreased from 37% at 14.5 min to 16% at 4 min, while the removal of D4 and hexane remained below 16%. The packing material was supplemented with 20% of activated carbon aiming at increasing the mass transfer of the most hydrophobic pollutants. This strategy supported high removal efficiencies of 43 and 45% for hexane and D5 at the lowest EBRT. CO_2 and silica were identified as mineralization products

along with the presence of metabolites in the trickling solution such as dimethylsilanediol, 2-carene and α-terpinene.

KEYWORDS

Activated carbon; Biogas upgrading; Biotrickling filter; Siloxanes;

1. INTRODUCTION

Global warming and climate change concerns have led the EU to set the Renewable Energy Directive (2009/28/EC) aiming to reduce greenhouse gas (GHG) emissions by incentivizing renewable energies over fossil fuels. As an alternative renewable energy, biogas is a promising and versatile source of energy that originates from the anaerobic digestion of a wide spectrum of organic wastes (Alvarez-Gaitan et al., 2016; Yu and Schanbacher, 2010). In this context, the production and exploitation of this methane-rich gas has increased in landfills and wastewater treatment plants (WWTP) as a result of its potential for electricity and heat production, injection into natural gas grids or use as vehicle fuel (Bachmann, 2015; Herbes et al., 2018). This renewable gas is typically composed of CH_4 (35-70%), CO_2 (15-50%) and low concentrations (<2%) of other biogas pollutants that influence the final use of biogas. Apart from volatile organic compounds (VOCs), siloxanes are getting an increasing attention as priority biogas pollutants. Siloxanes are a group of polymeric compounds of silicon and oxygen bonds with organic chains attached to the silicon atoms. The combustion reactions during the valorization of biogas in energy conversion systems (ERS) typically results in the transformation of volatile siloxanes into SiO_2 and microcrystalline quartz. The deposition of such compounds over different engine parts mediates abrasion and a

deterioration in heat conduction or lubrication (de Arespacochaga et al., 2014; Soreanu et al., 2011).

Adsorption technologies are the only commercially available platform for siloxanes removal, providing high removal efficiencies (Arespacochaga Santiago, 2015). Adsorption onto activated carbon (AC) or silica gel are the most widely used technology to abate siloxanes and VOCs from biogas. However, the replacement of the saturated adsorbent material entails high operational costs and environmental impacts (Cabrera-Codony et al., 2015). Emerging technologies such as biotrickling filtration (BTF) and membrane separation processes are currently under investigation to reduce the operating cost and environmental impact of conventional biogas upgrading technologies (Santos-Clotas et al., 2019a; Vergara-Fernández et al., 2018). In this sense, biotrickling filtration is based on biogas polishing using biofilms attached to inert packing materials (e.g. pall rings, lava rock) provided with nutrients and water by a trickling solution (either in co-current or counter-current mode to the biogas stream). BTF offers many advantages such as low pressure drops, simplicity in the operation and low operational costs, which make it more attractive and eco-friendlier than its physical-chemical counterparts and even than other biotechnologies (i.e. biofilters) (Malhautier et al., 2014).

Despite the advantages of BTFs, the number of publications investigating siloxane removal in BTFs is scarce and limited to a reduced number of siloxanes. The few studies reported in the literature demonstrated the biodegradability (Soreanu, 2016) of these compounds under aerobic conditions. Thus, Popat and Deshusses (2008) achieved a removal efficiency (RE) of D4 of 43% at 19.5 min of EBRT and REs of 50-60% at 30-40 min with O_2 as electron acceptor [7]. The same authors also investigated the

anaerobic removal of D4 in a BTF operated at 4 min of EBRT, obtaining a maximum RE of 15%. Likewise, Accettola *et al.* (2008) (Accettola et al., 2008) reported the aerobic degradation of hexamethylcyclotrisiloxane (D3) with a limited RE of 10-20% at 2-4 min of EBRT. More recently, Li et al., (2014) reported a 74% RE for D4 in an aerobic BTF operating at 13.2 min EBRT, identifying the benefits of rhamnolipids in the liquid phase produced by *Pseudomonas aeruginosa*. However, the low concentrations of O_2 in biogas (if any at all), together with its associated explosion risk, have limited the use of aerobic biotechnologies in biogas upgrading applications. In addition, there is consistent evidence in literature demonstrating the capability of BTFs to treat VOC-laden emissions from the petrochemical industry using nitrate as an alternative electron acceptor (Akmirza et al., 2017; Almenglo et al., 2016; Muñoz et al., 2013). In this context, the co-treatment of siloxanes and VOCs in bioreactors under anoxic conditions represents an unexplored technological platform to carry out the final polishing of biogas in a cost-effective and environmental-friendly way.

The low mas transfer of hydrophobic gas pollutants constitutes one of the major drawbacks challenging the bioavailability of substrates to the microorganisms and their subsequent biodegradation in biological processes (Cheng et al., 2016). In order to improve the biodegradation performance of BTFs for low water-soluble VOCs, several methods have been investigated including surfactant addition (Qian et al., 2018; Song et al., 2012; Tu et al., 2015), application of fungal biocatalysts (Zehraoui et al., 2013) and the use of hydrophilic compounds (Zehraoui et al., 2012). On the other hand, adsorption onto activated carbon is one of the most popular technologies to capture VOCs and several studies have reported on their high capacity to adsorb siloxanes.

The aim of the present work was to investigate the anoxic biodegradation of siloxanes (D4 and D5) in a lab-scale biotrickling filter in the presence of other biogas impurities, i.e. volatile organic compounds such as hexane, toluene and limonene. The influence of the EBRT on siloxane and VOC removal performance, along with the beneficial role of activated carbon (AC) supplementation in the BTF as a support (in order to enhance the mass transfer of biogas pollutants to the microbial community), were also investigated.

2. MATERIALS AND METHODS

2.1 BTF Inoculum

Anaerobic sludge from the mixed sludge anaerobic digester of the urban wastewater treatment plant of Rubí (Barcelona, Spain) was used as precursor inoculum in the biotrickling filter. The anaerobic sludge was centrifuged at 6000 rpm for 10 min and re-suspended in fresh synthetic mineral medium. This procedure was repeated several times in order to clean the sludge from dissolved organic matter. The BTF was first inoculated with 320 mL of anaerobic sludge and left recirculating for three days to promote biomass attachment to the lava rock. At day 43, the BTF was re-inoculated using a *Pseudomonas aeruginosa* strain isolated from anaerobic sludge samples by selective growth using the picking up method. The culture was incubated in liquid mineral salts medium containing D4 as a carbon source at 30 ºC and 125 rpm in an orbital shaker. After 72 hours, the inoculum was centrifuged and washed four times in mineral media without D4. The *P. aeruginosa* culture was finally re-suspended in 250 mL of synthetic mineral solution without residual organic compounds. The initial population density of *P. aeruginosa* culture was 4.06×10^6 cell mL^{-1}.

2.2 Experimental setup

A schematic of the lab-scale biotrickling filter setup designed and constructed for this study is shown in Fig. 1. The reactor consisted of a cylindrical glass column with an inner diameter of 6 cm and a total height of 46 cm. The packing material consisted of inert lava rock of 8-12 mm particle size. Different empty bed residence times of 4.0, 7.3, 10.1 and 14.5 min were evaluated. The reactor was operated in a counter-current flow configuration. A trickling solution of synthetic mineral salt medium was continuously recirculated by a peristaltic pump (Watson Marlow) from an external reservoir (250 cm^3) and sprayed through the top of the bed column at a rate of 47 cm h^{-1}. The total volume taking into account the piping as well as the reservoir accounted for roughly 400 cm^3. The trickling solution in the reservoir was renewed every 72h, which represented a dilution rate of 0.3 $days^{-1}$). The synthetic mineral medium used in this study was composed of: 1 g L^{-1} NaCl; 0.2 g L^{-1} $MgSO_4 \cdot 7H_2O$; 0.02 g L^{-1} $CaCl_2 \cdot 2H_2O$; 0.04 g L^{-1} NH_4Cl; 1.16 g L^{-1} $KH_2PO_4 \cdot H_20$; 4.76 g L^{-1} of HEPES buffering agent. The pH was adjusted to 6.9 using NaOH 1 M. All chemicals were obtained from PANREAC AppliChem with purities higher than 99%. Anoxic conditions were provided during the whole operation of the BTF by supplementing the mineral medium with 2 g L^{-1} $NaNO_3$ (NO_3^- acting as the final electron acceptor).

The feed gas flow was accurately regulated by a mass flow controller (Alicat Scientific) and mixed in four static mixers followed by a 1-L mixing chamber. Then, the stream was divided for the reactor inlet and a purge for analysis matters. The synthetic gas was generated by infusing the target compounds using a syringe pump (11 Elite, Harvard Apparatus) to a N_2 stream previously humidified in a water column. The mixture was

composed of octamethylcyclotetrasiloxane (D4, 98%), decamethylcyclopentasiloxane (D5, 97%), toluene (99.8%), D-limonene (97%) and n-hexane (99%) (Sigma Aldrich). The physicochemical properties of the target pollutants and their concentration in the multicomponent gas emission are detailed in Table 1.

The composition of the inlet and outlet gas emission of the BTF was analyzed via a flow-through gas sampling valve in a gas chromatograph equipped with a flame ionization detector (GC-FID, 7890B Agilent Technologies) and a HP-5ms Ultra Inert capillary column (Agilent Technologies). The oven temperature ramped from 60 ºC (1 min) to 120 ºC at 30 ºC min^{-1}, then to 150 ºC at 10 ºC min^{-1}, and finally to 300 ºC at 50 ºC min^{-1} and held for 3 min. The injector temperature was set at 240 ºC with helium (99.99% Abelló Linde, Spain) at a split ratio 1:6. Calibration was carried out using external standards prepared in the above described continuous set-up. Routine analysis of the inlet and outlet gas streams was performed in triplicate (coefficient of variation < 6%).

2.3 Operating conditions

The operation of the BTF was divided into four stages related to the carbon source provided in the gas stream and the type of packing material used in the BTF. Stage I (days 0-42) operated with a N_2 stream containing D4 at 62 ± 2 mg m^{-3} supplied at an EBRT of 14.5 min. In stage II (days 43-152), the target pollutant was switched to a multicomponent mixture of siloxanes (D4 and D5) and VOCs (hexane, toluene and limonene) in the concentrations described in Table 1. These biogas pollutants were selected based on an exhaustive database set up by Papadias et al., (2011) of published data on impurities found in the biogas produced by anaerobic digestion of sewage

sludge. Nearly 300 biogas contaminants were included and classified in different categories, with special attention into their concentration range. The most representative compounds among the most important biogas pollutant categories were selected: hexane from the class of alkanes, limonene from the class of cyclic hydrocarbons, toluene from the class of aromatic hydrocarbons, and D4 and D5 from the class of siloxanes.

During stage II, the influence of the EBRT (14.5, 10.1, 7.3 and 4 min) on the removal efficiency and elimination capacity of the target biogas contaminants was tested. The EBRT were selected according to literature (Popat and Deshusses, 2008) aiming at minimizing the reactor size required for siloxane biodegradation. In stage III (days 153-186), 35 g of a wood-based chemically activated carbon in pellet size (2-3 mm particle size) were added at the top of the packed bed, which accounted for a layer of approximately 5 cm of packing bed. The AC used in the present study was selected due to its high siloxane adsorption capacity as well as its capacity to transform siloxanes into α-ω-silanediols in the presence of moisture (Cabrera-Codony et al., 2018; Santos-Clotas et al., 2019b) Finally, the packing lava rock was removed from the column, and the biofiltration process was performed with the 5 cm layer of AC (introduced during Stage III) as the only packing bed (Stage IV, days 187-207). During stage II-4 and stage IV, the influence of the trickling solution dispersion on the performance of the BTF was evaluated by stopping (5 h) and re-starting the recirculation of the trickling solution. During these events, the outlet gas stream of the BTF was continuously monitored by GC-FID. An abiotic test was initially carried out to evaluate the physicochemical removal of siloxane D4 in the experimental set-up. Additional abiotic tests using the multicomponent gas mixture were performed in parallel lab-scale BTF.

2.4 Metabolites analysis and identification

2.4.1 Outlet emission

The BTF outlet gas was analyzed by GC-MS (7890B GC-5977B MS, Agilent Technologies) in order to identify CO_2 and volatile biodegradation products. CO_2 was determined by monitoring the ion with m/z 44 and calibration standards were prepared by diluting CO_2 (99.99%, Abelló Linde, Spain) to N_2. Limonene metabolites were identified by GC-MS analysis by comparing the m/z of the metabolites with those in the NIST library, and by injecting pure reagents (if commercially available) for further confirmation.

2.4.2 Trickling solution

Identification of the biodegradation metabolites in the trickling solution was carried out by GC-MS (7890B GC-5977B MS, Agilent Technologies). Silanediols determination procedure is reported elsewhere (Cabrera-Codony et al., 2017).

Silicic acid was measured by means of a colorimetric test in which dissolved silicic acid reacted with ammonium molybdate under acid conditions producing the yellow complex molybdosilicate acid. Oxalic acid was added to avoid the formation of molybdophosphate acid and therefore the interference of phosphates. The absorbance of the resulting samples was measured at 410 nm in a spectrophotometer (3100PC, VWR, USA). Total silicon concentration was analyzed by means of inductively coupled plasma-optical emission spectroscopy (ICP-OES, Agilent 5100).

2.4.3 Packing media

Samples of the lava rock and activated carbon were taken at different times for Scanning Electron Microscope (SEM) analysis in order to observe the biomass grown in

the packed bed of the BTF. Biomass in the samples was fixed with 2.5% (wt/vol) glutaraldehyde in 0.1 M cacodylate buffer (pH 7.4) at 4ºC for 4 h. Then, biomass samples were washed and dehydrated successively in ethanol, dried at the critical point CO_2 method (K 850 CPD, Emithech, Germany), and covered in carbon by the evaporation method with a turbo evaporator (K950, Emitrech, Germany). The analysis of the samples was carried out with a scanning electron microscope (S-4100 FE-SEM Hitachi, Japan). Digital images were collected and processed by Quartz PCI program.

On the other side, THF was used as solvent to extract polar and nonpolar species that remain adsorbed or biosorbed in the solid support and the biomass film. The extraction procedure and GC-MS identification analysis was previously reported (Cabrera-Codony et al., 2018).

3. RESULTS AND DISCUSSION

3.1 Lab-scale BTF start up

The experimental set-up was initially operated abiotically to assess the physico-chemical processes underlying D4 removal from the synthetic gas emission. The D4 concentration at the outlet of the BTF, which was measured by GC-FID after 72 h of abiotic operation, matched the inlet D4 concentration, which ruled out the occurrence of significant abiotic siloxane removal mechanisms. The low D4 aqueous solubility mediated a rapid equilibrium between the gas and liquid phases in the BTF, which explains the similar concentrations in the inlet and outlet emissions.

The lab-scale biotrickling filter was inoculated with anaerobic sludge from an urban wastewater treatment plant. D4 biodegradation under anoxic conditions in WWTPs was

previously described (Xu et al., 2013), with microbial catalytic hydrolysis of cyclic siloxanes identified as one of the main degradation pathways. The system was run for 36 days at a D4 inlet load of 0.26 g m^{-3} h^{-1} (Stage I), which resulted in a steady state removal efficiency (RE) of 14%.

A sample of the bed material was collected to explore the biofilm grown in the lava rock used as packing material. SEM images revealed the presence of rod-shaped bacterial cells in the size range 1-3 μm attached on the surface of the packing rock. The population was not quantified, thought it could be observed that the lava rock structure was hardly noticed due to the high colonization of bacteria. A thorough microbial community analysis of the biofilm established in the BTF was recently reported by Boada et al., (2018). According to the gene sequencing analysis of the biofilm samples, species from the phylum *Proteobacteria* and *Actinobacteria* were identified, including *Rhodococcus* sp., *Methylibium* sp. and *Pseudomonas aeruginosa*. Of them, *P. aeruginosa* is a facultative anaerobe that can proliferate with nitrate as a terminal electron acceptor and has been described as a siloxane-biodegrading species capable of producing biosurfactant molecules (Li et al., 2014; Rahman et al., 2002; Rościszewski et al., 1998).

3.2 BTF operation with a multicomponent mixture (Stage II)

Based on the microbial analysis conducted in stage I, a concentrated culture of *P. aeruginosa* was used to re-inoculate the BTF at day 43 in order to boost the siloxane removal capacity of the system. The feed gas composition was switched to a multicomponent mixture of siloxanes (D4 and D5) and VOCs (toluene, limonene and

hexane) typically found in sewage biogas (Papadias et al., 2011). Abiotic tests with the multicomponent mixture were performed in a twin parallel BTF in the same conditions. From these tests (results not shown) it was observed that no abiotic removal of the target pollutants occurred. Fig. 2 plots the removal efficiency (RE) and the elimination capacity (EC) of the biogas contaminants during the entire operation. The system was operated at an EBRT of 14.5 min until day 86. The outlet concentrations of toluene and limonene during state II-1 remained below the detection limit of the analytical method (0.5 mg m^{-3} for both compounds). Thus, a complete removal of toluene and limonene was achieved almost immediately (Fig. 2B and 3C, Stage II-1), which remained stable during the whole operation. Thus, the steady state elimination capacities (EC) accounted for 0.10 ± 0.002 and 0.83 ± 0.009 g m^{-3} h^{-1} for toluene and limonene, respectively. However, hexane EC during stage II-1 averaged 0.21 ± 0.02 g m^{-3} h^{-1}, which corresponded to a removal efficiency up to 14% (Fig. 2A). *Pseudomonas* sp., the dominant specie in the biofilm community, was capable of degrading hexane to some extent, although this biodegradation was limited by pollutant mass transport as a result of its high Henry's law coefficient. On the other hand, the removal efficiency of the target siloxanes increased after 15 days of acclimation of the microbial communities to the multicomponent gas emission (Fig. 2D and 2D days 55-70). Stable REs of 13% for D4 and 37% for D5 were achieved, which corresponded to ECs of 0.03 ± 0.009 and 0.14 ± 0.003 g m^{-3} h^{-1}, respectively.

The EBRT was decreased to 10.1 min in Stage II-2 (days 86-107). The RE of toluene and limonene remained at ~100 % for both compounds, whereas their ECs increased to 1.19 ± 0.002 and 0.14 ± 0.001 g m^{-3} h^{-1}, respectively. Hexane RE did not significantly vary, although its EC increased to 0.29 ± 0.003 g m^{-3} h^{-1}. On the other hand, the REs of

D4 slightly decreased to 13 and 30%, while their ECs incremented up to 0.04 ± 0.004 and 0.16 ± 0.001 g m^{-3} h^{-1}. Thus, the capacity of the bioreactor to remove toluene and limonene was not hampered by a further decrease of the EBRT to 7.3 min in Stage II-3 (days 108-128), whose ECs were incremented up to 0.19 ± 0.002 g m^{-3} h^{-1} for toluene and 1.66 ± 0.001 g m^{-3} h^{-1} for limonene. The REs for hexane, D4 and D5 were slightly reduced to 11, 9 and 21%, respectively. The EC for hexane increased to 0.34 ± 0.005, while the EC of the two target siloxanes remained quite similar compared to the previous stage (0.04 ± 0.002 and 0.17 ± 0.001 g m^{-3} h^{-1} for D4 and D5, respectively).

Finally, the EBRT was further decreased to 4 min in Stage II-4 (days 129-152). In this context, while toluene and limonene were still not detected in the outlet gas stream, hexane REs decreased to 8% (corresponding to an EC of 0.45 ± 0.004 g m^{-3} h^{-1}). The REs of D4 and D5 were also reduced, although their ECs increased up to 0.06 ± 0.009 g m^{-3} h^{-1} for D4 and 0.23 ± 0.003 g m^{-3} h^{-1}.

Overall toluene and limonene were completely eliminated regardless of the EBRT, exhibiting ECs of up to 3 ± 0.003 g m^{-3} h^{-1} and 0.35 ± 0.001 g m^{3} h^{-1}, respectively at the lowest EBRT (Fig. 3). Hexane's removal efficiency remained stable over the tested range of EBRTs, with ECs up to 0.45 g m^{-3} h^{-1}. On the other hand, the decrease in the EBRT resulted in more remarkable decrease in the RE of D5 compared to D4, which also experienced an increase in ECs up to 0.23 ± 0.003 and 0.06 ± 0.009 g m^{-3} h^{-1}, respectively. The results obtained confirmed that the removal of the target compounds was correlated with their Henry's law constants, which pointed out that the performance of the BTF was limited by the mass transport of hexane, D4 and D5 from the gas to the microbial community.

3.3 The role of activated carbon on the BTF performance (Stage III)

A layer of 5 cm of activated carbon was added at the top of the lava rock in the BTF by day 153 (Stage III) in order to improve the removal of siloxanes, which increased the EBRT up to 12 min (10 min corresponding to lava rock and 2 min to the AC layer). Some reports have pointed out the capability of the oxygen functional groups present in the surface of porous carbons to promote hydrolysis reactions leading to ring-opening and the formation of α-ω-silanediols (Cabrera-Codony et al., 2018), which are more water soluble compounds than cyclic methyl siloxanes. Thus, a phosphoric acid chemical activated carbon was chosen for this purpose according to previous investigations on siloxane adsorption (Santos-Clotas et al., 2019b).

Only the two target siloxanes and hexane were detected in the outlet of the BTF during stage III. The outlet concentration of the three compounds with the lowest REs rapidly dropped to negligible values when the activated carbon was added, likely due to physical adsorption (Fig. 4). However, a fast breakthrough was recorded: it took 250 min to reach the previous outlet concentration, i.e. the maximum possible Si uptake during this period of time was of 0.03 mg g_{AC}^{-1}. Considering that the adsorption capacity of the activated carbon used, explored in previous investigations (Cabrera-Codony et al., 2018; Santos-Clotas et al., 2019b), is in the range of 60-170 mg Si g_{AC}^{-1}, the AC was far from being saturated, suggesting that adsorption of both siloxanes and hexane in soaked activated carbon was negligible.

Interestingly, the beneficial role of activated carbon on hexane and D5 was evident after an acclimation period of 20 days (Fig. 2 from day 170 on). Indeed, the removal efficiency of hexane increased up to steady state values of 43 ± 2 %. Previous investigations on the biodegradation of hexane by *Pseudomonas aeruginosa* identified

that mass transfer limited the performance of bioreactors, which encouraged the use of organic solvents to enhance the availability of this hydrophobic gas pollutant (Muñoz et al., 2006). In this investigation, the mass transfer of hexane to the biofilm was thereby enhanced with the addition of activated carbon as a support.

The impact of activated carbon addition on siloxane removal depended on the type of siloxane. Thus, while D4 removal efficiency remained stable at 16% during stage III, D5 RE gradually increased up to steady state values of 45%. D5 affinity for chemically activated carbons was found stronger than that of D4 and other siloxanes in previous works, as well as its proneness to transformation into α-ω-silanediols in the presence of moisture (Cabrera-Codony et al., 2018). In this context, the higher degradation of D5 could be related to the activated carbon layer, which supported the ring-opening polymerization of siloxane D5 and its transformation into more water-soluble compounds (i.e. α-ω-silanediols), eventually enhancing their mass transfer towards the biofilm.

3.4 Activated carbon as biomass support in BTF (Stage IV)

The activated carbon surface was analyzed at day 180 using scanning electron microscopy to observe the microbial population. SEM pictures revealed the carbon surface heterogeneously colonized by microorganisms, where the cracks and fissures in the rough surface of granular activated carbon served as effective spots for biofilm formation (Kalkan et al., 2011). Thus, after ensuring that biofilm was formed over the AC surface, the lava rock was completely removed from the reactor, which entailed that the 5 cm layer of activated carbon was the only packing material in the BTF and the

EBRT decreased to 2 min (Stage IV). In this context, while toluene removal was complete, limonene RE decreased to 78% at the beginning of stage IV. This initial decrease in the RE of this monoterpene was likely mediated by the absence in the AC of a microbial community capable of degrading limonene, which was completely degraded throughout the lava rock layer during Stage II, and therefore prevented the exposure of the top AC-layer to limonene in Stage III. Thus, the microbial community already acclimated to limonene was also cleared from the BTF when removing the lava rock. However, the RE of limonene reached 100 % within the next 3 days from re-packing of the BTF, which highlighted the high robustness of the system and the rapid acclimation of the microbial community to VOCs. The lava rock evacuation and its associated decrease in the EBRT to 2 min resulted in a sharp decrease in D5 removal efficiency from 43% at the beginning of stage IV to steady stated values of 22. D5 abatement in the BTF during steady state was likely due to a combination of microbial degradation boosted by an enhanced siloxane adsorption and hydrolysis mediated by the activated carbon. Overall, the BTF packed with a thin layer of activated carbon (corresponding to an EBRT of 2 min) achieved comparable removal efficiencies to those recorded in the BTF packed with a 6 times larger of lava rock bed (Fig. 3, EBRT 14.5 min). The AC was an effective packing material for cell attachment as well as an efficient packing material for the final polishing of biogas. This study also confirmed that a short bed of AC (i.e. low EBRT) would entail smaller bioreactor volume than the lava rock, which will significantly decrease the capital and operating cost of biogas. The results herein obtained also suggest that a supplementary adsorption treatment would be required for complete siloxanes removal. The complete removal achieved for the target VOCs in the lava rock bed is particularly relevant since toluene and limonene are major competitors

for adsorptive sites in current biogas adsorption technologies (Cabrera-Codony et al., 2018). A complete VOC removal in an anoxic BTF prior a final adsorption polishing step, together with the partial siloxane biodegradation, might extend the lifetime of adsorption filters, which would ultimately decrease the operational costs of biogas upgrading.

3.5 Processes governing siloxane removal

In stages II and III the GC-MS analysis of the outlet gas did not detect significant amount of volatile metabolites. In this context, the trickling solution was analyzed to determine the presence of soluble transformation products during the operation with lava rock (Stage II-4) and lava rock and AC (Stage III). Acid silicic concentrations of 7.3 and 10.6 mg Si L^{-1} were recorded during stage II-4 and III, respectively. Moreover, GC-MS qualitative analysis revealed the presence of dimethylsilanediol (DMSD), tetramethyl-1,3-disiloxanediol and hexamethyl-1,5-trisiloxanediol (Table 2) in the trickling liquid of stage III. Only the first two silanediols compounds were identified at lower concentrations in the trickling solution during stage II-4. These results agree with the higher removal efficiency of D5 achieved under BTF operation with an activated carbon packed bed. This siloxane transformation products are formed by both i) bond cleavage of D4 and D5 through hydrolysis reactions promoted by AC's functional groups, and ii) biodegradation of larger α-ω-silanediols, D4 and D5. Thus, the higher concentration found was the consequence of both the AC catalytic activity and biodegradation, which would eventually support the hypothesis of the ability of ACs to catalyze the ring-opening of cyclic siloxanes and thus boost siloxane degradation (Cabrera-Codony et al., 2014). Since silanediols could not be quantified due to lack of

commercial reagents, total Si analysis were performed by ICP-OES aiming at closing the Si mass balance. Si contents of 13.2 and 21.8 mg L^{-1} were obtained in the trickling solution of Stages II-4 and III, respectively. For the mass balance, it was taken into account that the liquid samples were collected after 3 days (when the recirculation media was replaced) and a total liquid volume of roughly 400 cm^3. The Si analyses accounted for a 22 and 36% of the total Si that entered the reactor and was found dissolved in the recirculation liquid of Stages II-4 and III, respectively. Moreover, according to the average REs obtained for both D4 and D5 in the different stages, a 74 and 65% of Si was found in the outlet emissions in Stage II-4 and III, respectively, which mostly completed the Si mass balance. The remaining percentage of Si to reach 100 was below 4% in both stages, which could be attributed to the inlet concentration stability as well as the accurate liquid volume in the system. In this context, siloxane removal was likely due to mainly biodegradation in stage II-4. In stage III biodegradation would still be the major process involved, though boosted by transformation reactions due to the AC surface, as observed with the higher presence of Silicon soluble species.

On the other hand, in stage IV the use of activated carbon as biomass support drastically increased the elimination capacity of siloxanes (Fig. 2). Thus, the removal efficiency of the system remained stable despite the reduction of the EBRT from 14.5 min (Stage I) to 2 min. In order to get a further insight on the mechanisms governing siloxane removal, activated carbon samples were collected at the end of Stage IV to analyze the compounds adsorbed or retained in the biofilm. THF extraction was performed following the experimental procedure previously described (Cabrera-Codony et al., 2018). The results showed that the siloxane retained in the solid phase was in a

concentration below the quantification limit (<0.5 mg m^{-3}). Considering the total volume of the packing material and the amount of siloxane circulated during the whole stage, both physicochemical adsoption and biosorption of siloxane removal could be ruled out.

While no volatile silicon byproducts were detected in the gas outlet, the CO_2 production during Stage IV was monitored. An average concentration of CO_2 up to 405 ppm_v was detected, which corresponded to 21 g h^{-1} $m_{reactor}^{-3}$. This CO_2 production corresponded to an average pollutant mineralization of 80% considering both the siloxanes and VOCs removed. Such incomplete mineralization determined by the CO_2 analysis could be linked to the accumulation of methyl-siloxane by-products in the liquid phase as well as the growth of new biomass. Therefore, these results supported the hypothesis that biodegradation was the predominant process involved in the removal of VOCs and siloxanes.

3.6 Robustness of AC as BTF support

In order to assess the impact of the trickling solution dispersion on the performance of the BTF, the recirculation of the trickling solution was paused during periods of ca. 5 hours and re-started. While toluene and limonene were completely removed during the trickling dispersion period, both biogas pollutants were detected in the exhaust gas in the absence of mineral medium dispersion likely due to the limitation in nitrate availability, which was the only final electron acceptor in the biodegradation process. Moreover, biodegradation metabolites from the incomplete mineralization of limonene were detected in the outlet emission. Fig. 5A depicts the outlet/inlet areas ratios (C/C_0)

for toluene, limonene and metabolites during the stop and resumption of the trickling solution. After 5 h of trickling solution shutdown, the C/C_o ratios for toluene and limonene reached 0.7 and 0.46, while a complete removal of both pollutants and metabolites was recorded after the resumption of liquid distribution. GC-MS analysis of the outlet gas in the absence of trickling medium dispersion identified 2-carene and α-terpinene (Table 2) as the main metabolites released during the incomplete oxidation of limonene in the absence of NO_3^-. Moreover, a qualitative analysis by GC-MS of the trickling solution revealed traces of p-cymene, which could have also originated from the partial oxidation of limonene.

On the other hand, Fig. 5B shows the performance of the BTF packed with activated carbon (stage IV) during an event of trickling dispersion stoppage. During the 5-hour trickling solution shutdown, the removal efficiency of both toluene and limonene remained at 100 % and no metabolite was detected in the outlet gas emission. It needs to be highlighted that, as visually noticed, the carbon layer remained highly humidified during the period without mineral medium distribution, which was not observed during the same experiment with lava rock. This finding suggested that the porous AC was capable of retaining sufficient amount of trickling solution to provide the biofilm with the necessary compounds to maintain microbial activity during periods without trickling solution distribution. Using AC as packing material in anoxic BTF may guarantee a sustained electron acceptor availability to the biofilm compared to conventional packing media, which are dependent on stable dispersion conditions.

4. CONCLUSIONS

This study confirmed the potential of biotrickling filtration to remove siloxanes and VOC under anoxic conditions. Toluene and limonene were effectively degraded at all

the EBRT tested. The use of activated carbon as packing material to overcome mass transfer limitation encountered for hexane, D4 and D5 supported an effective biomass growth, while promoting hydrolysis reactions leading to soluble silanediols. Furthermore, AC supplementation enabled the BTF operation at reduced EBRTs, which would ultimately decrease the operating and investment cost of biogas purification. This study also demonstrated a high robustness towards variations in the EBRT and interruptions in the trickling solution distribution.

E-supplementary data for this work can be found in e-version of this paper online

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5. REFERENCES

1. Accettola, F., Guebitz, G.M., Schoeftner, R., 2008. Siloxane removal from biogas by biofiltration: Biodegradation studies. Clean Technol. Environ. Policy 10, 211–218. https://doi.org/10.1007/s10098-007-0141-4

Akmirza, I., Pascual, C., Carvajal, A., Pérez, R., Muñoz, R., Lebrero, R., 2017. Anoxic biodegradation of BTEX in a biotrickling filter. Sci. Total Environ. 587–588, 457–465. https://doi.org/10.1016/j.scitotenv.2017.02.130

Almenglo, F., Ramírez, M., Gómez, J.M., Cantero, D., 2016. Operational conditions for start-up and nitrate-feeding in an anoxic biotrickling filtration process at pilot scale. Chem. Eng. J. 285, 83–91. https://doi.org/10.1016/j.cej.2015.09.094

Alvarez-Gaitan, J.P., Short, M.D., Lundie, S., Stuetz, R., 2016. Towards a comprehensive greenhouse gas emissions inventory for biosolids. Water Res. 96, 299–307. https://doi.org/10.1016/j.watres.2016.03.059

Arespacochaga Santiago, N. de, 2015. Sewage biogas energy valorization via solid oxide fuel cells. TDX (Tesis Dr. en Xarxa).

Bachmann, N., 2015. Sustainable biogas production in municipal wastewater treatment plants. IEA Bioenergy 20.

Boada, E., Santos-Clotas, E., Cabrera-Codony, A., Martin, M.J., Bañeras, L., Gich, F., 2018. Isolation of bacterial species with potential capacity siloxane removal in biogas upgrading, in: 2nd International Conference on Bioresource Technology for Bioenergy, Bioproducts & Environmental Sustainability (BIORESTEC2018). Sitges, Spain.

Cabrera-Codony, A., Georgi, A., Gonzalez-Olmos, R., Valdés, H., Martín, M.J., 2017. Zeolites as recyclable adsorbents/catalysts for biogas upgrading: Removal of octamethylcyclotetrasiloxane. Chem. Eng. J. 307. https://doi.org/10.1016/j.cej.2016.09.017

Cabrera-Codony, A., Gonzalez-Olmos, R., Martín, M.J., 2015. Regeneration of siloxane-exhausted activated carbon by advanced oxidation processes. J. Hazard. Mater. https://doi.org/10.1016/j.jhazmat.2014.11.053

Cabrera-Codony, A., Montes-Morán, M.A., Sánchez-Polo, M., Martín, M.J., Gonzalez-Olmos, R., 2014. Biogas upgrading: Optimal activated carbon properties for siloxane removal. Environ. Sci. Technol. 48. https://doi.org/10.1021/es501274a

Cabrera-Codony, A., Santos-Clotas, E., Ania, C.O., Martín, M.J., 2018. Competitive siloxane adsorption in multicomponent gas streams for biogas upgrading. Chem. Eng. J. 344. https://doi.org/10.1016/j.cej.2018.03.131

Cheng, Y., He, H., Yang, C., Zeng, G., Li, X., Chen, H., Yu, G., 2016. Challenges and solutions for biofiltration of hydrophobic volatile organic compounds. Biotechnol. Adv. 34, 1091–1102. https://doi.org/10.1016/j.biotechadv.2016.06.007

de Arespacochaga, N., Valderrama, C., Mesa, C., Bouchy, L., Cortina, J.L., 2014. Biogas deep clean-up based on adsorption technologies for Solid Oxide Fuel Cell applications. Chem. Eng. J. 255, 593–603. https://doi.org/10.1016/j.cej.2014.06.072

Herbes, C., Halbherr, V., Braun, L., 2018. Factors influencing prices for heat from biogas plants. Appl. Energy 221, 308–318. https://doi.org/10.1016/j.apenergy.2018.03.188

Kalkan, Ç., Yapsakli, K., Mertoglu, B., Tufan, D., Saatci, A., 2011. Evaluation of Biological Activated Carbon (BAC) process in wastewater treatment secondary ef fl uent for reclamation purposes. DES 265, 266–273. https://doi.org/10.1016/j.desal.2010.07.060

Li, Y., Zhang, W., Xu, J., 2014. Siloxanes removal from biogas by a lab-scale biotrickling filter inoculated with Pseudomonas aeruginosa S240. J. Hazard. Mater. 275, 175–184. https://doi.org/10.1016/j.jhazmat.2014.05.008

Malhautier, L., Quijano, G., Avezac, M., Rocher, J., Fanlo, J.L., 2014. Kinetic characterization of toluene biodegradation by Rhodococcus erythropolis: Towards a rationale for microflora enhancement in bioreactors devoted to air treatment. Chem. Eng. J. 247, 199–204. https://doi.org/10.1016/j.cej.2014.02.099

Muñoz, R., Arriaga, S., Hernández, S., Guieysse, B., Revah, S., 2006. Enhanced hexane biodegradation in a two phase partitioning bioreactor: Overcoming pollutant transport limitations. Process Biochem. 41, 1614–1619. https://doi.org/10.1016/j.procbio.2006.03.007

Muñoz, R., Souza, T.S.O., Glittmann, L., Pérez, R., Quijano, G., 2013. Biological anoxic treatment of O2-free VOC emissions from the petrochemical industry: A proof of concept study. J. Hazard. Mater. 260, 442–450. https://doi.org/10.1016/j.jhazmat.2013.05.051

Papadias, D., Ahmed, S., Kumar, R., 2011. Fuel Quality Issues in Stationary Fuel Cell Systems.

Popat, S.C., Deshusses, M. a., 2008. Biological removal of siloxanes from landfill and digester gases: Opportunities and challenges. Environ. Sci. Technol. 42, 8510–8515. https://doi.org/10.1021/es801320w

Qian, H., Cheng, Y., Yang, C., Wu, S., Zeng, G., Xi, J., 2018. Performance and biofilm characteristics of biotrickling filters for ethylbenzene removal in the presence of saponins. Environ. Sci. Pollut. Res. 25, 30021–30030. https://doi.org/10.1007/s11356-017-0776-6

Rahman, K.S.M., Rahman, T.J., McClean, S., Marchant, R., Banat, I.M., 2002. Rhamnolipid biosurfactant production by strains of Pseudomonas aeruginosa using low-cost raw materials. Biotechnol. Prog. 18, 1277–1281. https://doi.org/10.1021/bp020071x

Rościszewski, P., Łukasiak, J., Dorosz, A., Galiński, J., Szponar, M., 1998. Biodegradation of polyorganosiloxanes. Macromol. Symp. 130, 337–346. https://doi.org/10.1002/masy.19981300129

Santos-Clotas, E., Cabrera-Codony, A., Castillo, A., Martín, M.J., Poch, M., Monclús, H., 2019a. Environmental Decision Support System for Biogas Upgrading to Feasible Fuel. Energies 12, 1546. https://doi.org/10.3390/en12081546

Santos-Clotas, E., Cabrera-Codony, A., Ruiz, B., Fuente, E., Martín, M.J., 2019b. Sewage biogas efficient purification by means of lignocellulosic waste-based

activated carbons. Bioresour. Technol. 275, 207–215. https://doi.org/10.1016/j.biortech.2018.12.060

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

Soreanu, G., 2016. Insights into siloxane removal from biogas in biotrickling filters via process mapping-based analysis. Chemosphere 146, 539–546. https://doi.org/10.1016/j.chemosphere.2015.11.121

Soreanu, G., Béland, M., Falletta, P., Edmonson, K., Svoboda, L., Al-Jamal, M., Seto, P., 2011. Approaches concerning siloxane removal from biogas - A review. Can. Biosyst. Eng. / Le Genie des Biosyst. au Canada 53.

Tu, Y., Yang, C., Cheng, Y., Zeng, G., Lu, L., Wang, L., 2015. Effect of saponins on n-hexane removal in biotrickling filters. Bioresour. Technol. 175, 231–238. https://doi.org/10.1016/j.biortech.2014.10.039

Vergara-Fernández, A., Yánez, D., Morales, P., Scott, F., Aroca, G., Diaz-Robles, L., Moreno-Casas, P., 2018. Biofiltration of benzo[A]pyrene, toluene and formaldehyde in air by a consortium of Rhodococcus erythropolis and Fusarium solani: Effect of inlet loads, gas flow and temperature. Chem. Eng. J. 332, 702–710. https://doi.org/10.1016/j.cej.2017.09.095

Xu, L., Shi, Y., Cai, Y., 2013. Occurrence and fate of volatile siloxanes in a municipal Wastewater Treatment Plant of Beijing, China. Water Res. 47, 715–724. https://doi.org/10.1016/j.watres.2012.10.046

Yu, Z., Schanbacher, F.L., 2010. Production of Methane Biogas as Fuel Through Anaerobic Digestion, in: Singh, O. V, Harvey, S.P. (Eds.), Sustainable Biotechnology: Sources of Renewable Energy. Springer Netherlands, Dordrecht, pp. 105–127. https://doi.org/10.1007/978-90-481-3295-9_6

Zehraoui, A., Hassan, A.A., Sorial, G.A., 2013. Biological treatment of n-hexane and methanol in trickle bed air biofilters under acidic conditions. Biochem. Eng. J. 77, 129–135. https://doi.org/10.1016/j.bej.2013.06.001

Zehraoui, A., Hassan, A.A., Sorial, G.A., 2012. Effect of methanol on the biofiltration of n-hexane. J. Hazard. Mater. 219–220, 176–182. https://doi.org/10.1016/j.jhazmat.2012.03.075

Figure captions:

Fig. 1. Biotrickling filter setup (1 Syringe pump; 2 and 3 Mass flow controllers; 4 Water column; 5 Static mixers; 6 Mixing chamber; 7 Biotrickling filter; 8 Mineral media tank; 9 Peristaltic pump; 10 and 11 Sampling points).

Fig. 2. Time course of removal efficiency (RE, ●) and elimination capacity (EC, □) of hexane (A), toluene (B), limonene (C), D4 (D), and D5 (E) in the biotrickling filter. Vertical dashed lines represent changes in the operational conditions: empty bed residence times (EBRT) from 14.5>10.1>7.3>4 min, activated carbon addition (AC) and lava rock (LR) withdrawal.

Fig. 3. Effect of the empty bed residence time on the removal efficiency (A) and elimination capacity (B) of D4 (●), D5 (○), toluene (▲), limonene (□) and hexane (×).

Fig. 4. (A) Effect of the addition of activated carbon at day 153 in Stage III (represented by the dashed line) on the outlet stream concentrations of hexane (○), D4 (●) and D5 (□).

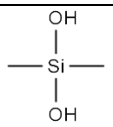
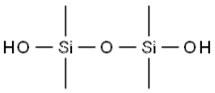
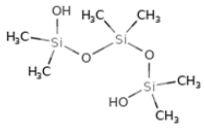
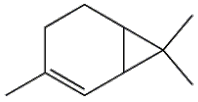
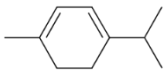
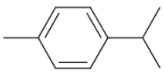
Fig. 5 Time-course of toluene (▲) and limonene (□) and the Gas Chromatograph response in area units of the metabolites (●) in the outlet gas, vertical dashed lines indicate the stoppage of the trickling recirculation, and vertical solid lines display the re-start of the recirculation. Data corresponding to stage II-1 with lava rock as packing material (A) and stage IV with AC (B).

Table 1. Physicochemical properties of the reagents provided by the manufacturer's data sheet (SigmaAldrich) and concentration on the test gas used in Stages II-IV of this work.

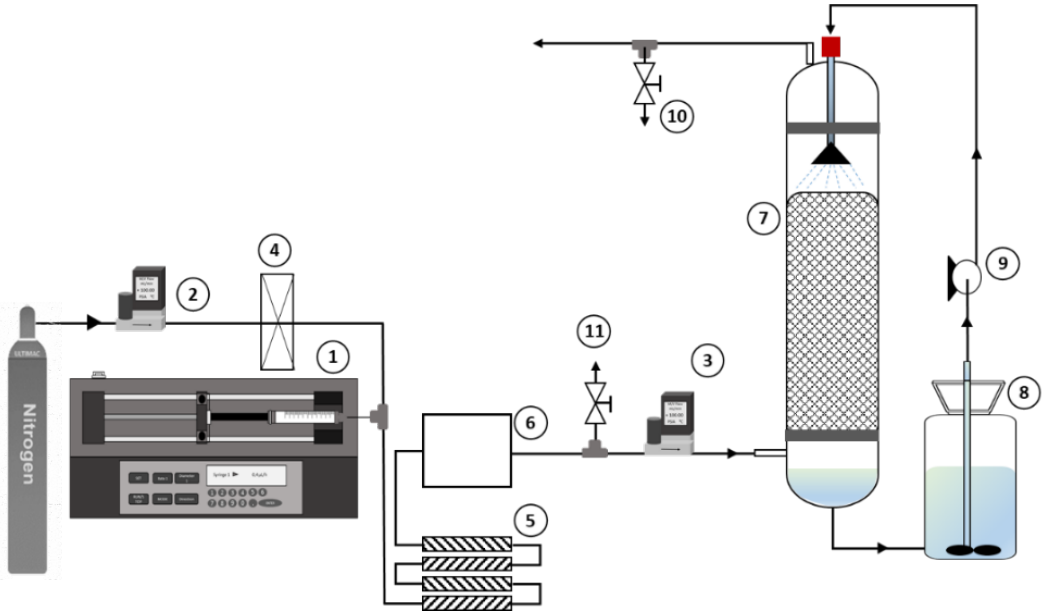
Compound	Molecular formula	Molecular weight [g mol^{-1}]	Solubility[a] [mg L^{-1}]	P_{vap} at 25ºC (mm Hg)	C_0[b] [mg m^{-3}]
Hexane	C_6H_{14}	86.2	9.5	153.0	375 ± 18
Toluene	C_7H_8	92.1	526	28.4	24 ± 2
Limonene	$C_{10}H_{16}$	136.2	13.8	2.1	220 ± 11
D4	$C_8H_{24}Si_4O_4$	296.6	0.056	1.1	54 ± 3
D5	$C_{10}H_{30}Si_5O_5$	370.8	0.017	0.2	102 ± 4

[a]In water at 25 ºC
[b]Feed gas concentration

Table 2. Metabolites identified by GC-MS during the biotrickling filter operation

Metabolite [abbreviation]	**Molecular weight** [g mol^{-1}]	**Chemical formula**	**Analytical ions m/z** [abundance*]
Dimethylsilanediol [DMSD]	92.2		77 [99.9] 45 [14.6] 78 [6.6]
Tetramethyl-1,3-disiloxanediol	166.3		133 [99.9] 151 [71.2] 135 [22.6]
Hexamethyl-1,5-trisiloxanediol	240.5		207 [99.9] 208 [21.1] 209 [17.0]
2-carene	136.2		93 [99.9] 121 [96.8] 136 [66.9]
α-Terpinene	136.2		121 [99.9] 93 [84.7] 136 [42.6]
p-cymene	134.2		119 [99.9] 91 [34.7] 134 [23.8]

*Abundance – relative intensity of each ion peak in % to the maximum ion intensity



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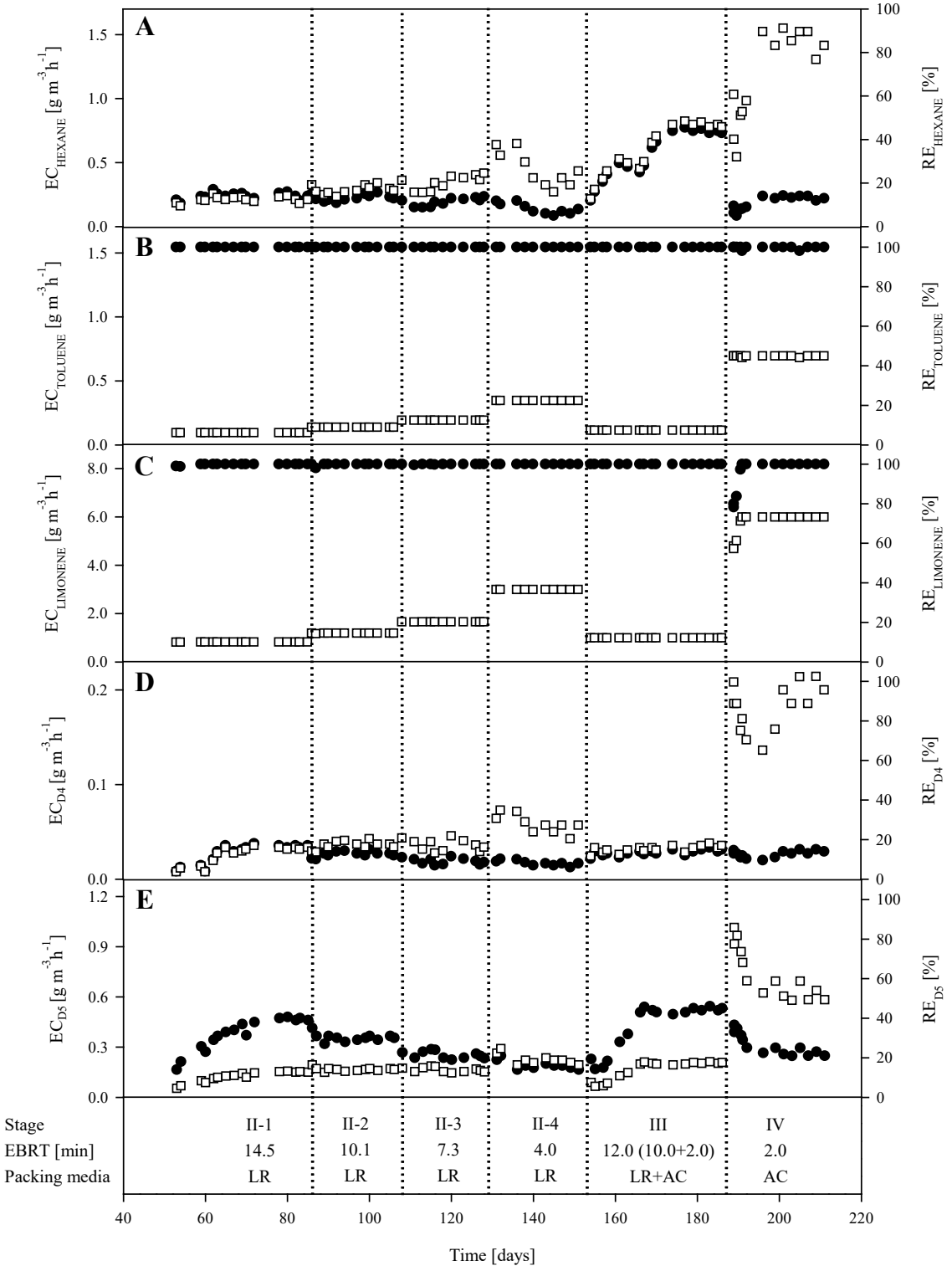

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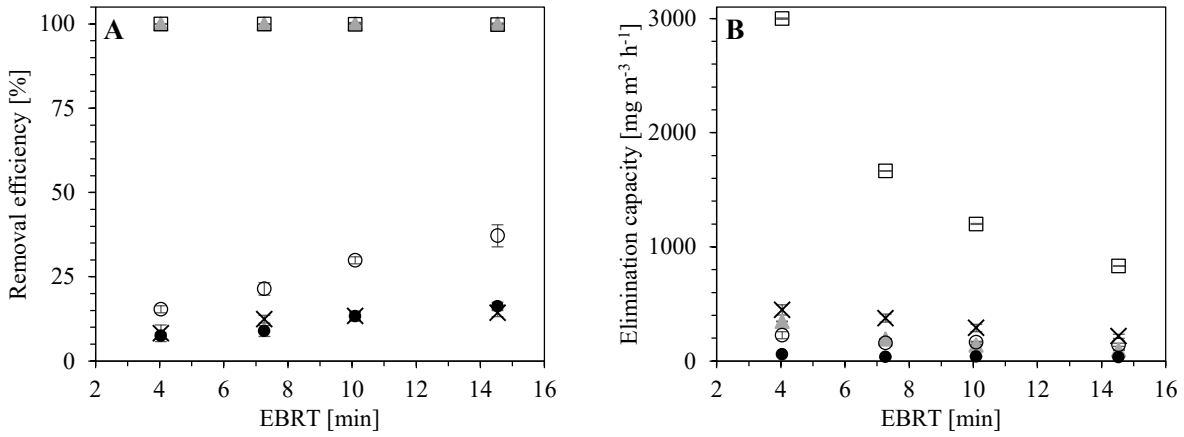
lines represent changes in the operational conditions: Empty bed residence time (EBRT) from 14.5>10.1>7.3>4 min, activated carbon addition (AC) and lava rock (LR) withdrawal.



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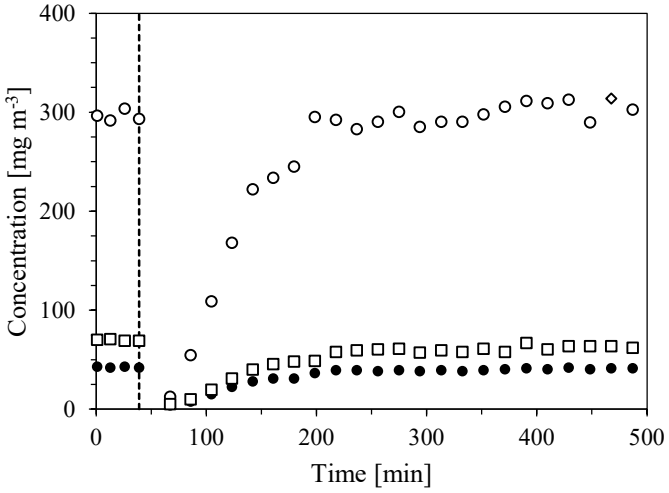

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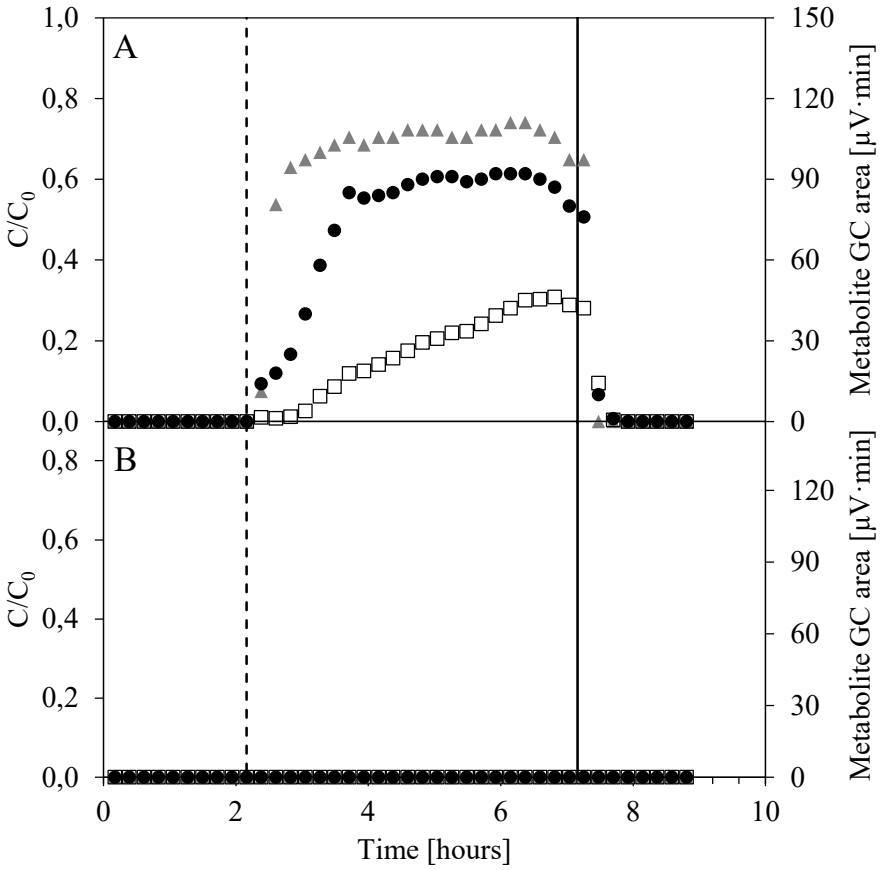

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