

Coupling adsorption with biotechnologies for siloxane abatement from biogas

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ABSTRACT

Biogas generated during anaerobic digestion in sewage plants contains a wide spectrum of trace impurities. Siloxanes are the most hazardous pollutants and its removal is mandatory for most energy applications. The most widely used technology is adsorption onto activated carbon (AC) despite the high operating costs. In this context, the use of biotechnologies to abate biogas pollutants could assist extending the lifetime of the AC filters. The present work evaluated at lab-scale the potentialities of implementing a biotrickling filter (BTF) before the adsorption technology. Moreover, the use of ACs with different characteristics and price was evaluated considering their selectivity towards siloxane over volatile organic compounds (VOCs). The pre-treatment of biogas in a BTF capable of eliminating VOCs like limonene increased significantly the adsorbent performance, reaching $690 \text{ m}^3 \text{ L}^{-1}$ of biogas treated per bed volume by a phosphoric-activated carbon, a six-fold increase in the performance of currently used materials in adsorption treatment. In terms of cost, a steam-activated coal-based with a major mesoporosity contribution implied the lowest operating costs reaching $2.3 \text{ €} (1000 \text{ m}^3_{\text{treated}})^{-1}$. Coupling BTF with adsorption into this same AC resulted in lower annual costs than adsorption alone due to the frequent replacements required when biogas was not pre-polished.

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1. Introduction

Anaerobic digestion has proved to be one of the most suitable processes to treat the high amounts of sludge generated in wastewater treatment plants (WWTP). The biological digestion of organic matter in the absence of O_2 leads to the generation of biogas, mainly composed by CH_4 (35–70%) and CO_2 (15–50%) [1], which, depending on the upgrading process undergone, can be used as fuel to produce heat or electricity, injected into the gas grid or used as a vehicle fuel. Despite other by-product gases like H_2S , N_2 or NH_3 , biogas also contains aromatic hydrocarbons, alkanes and alkenes, halogenated compounds and volatile methyl siloxanes [2,3].

Siloxanes are a group of polymeric organic silicones with Si–O–Si linkages composing either linear or cyclic molecules. They are widely used in many industrial and commercial applications given their water repelling properties, low surface tension, thermal conductivity and high flexibility as well as resistance to temperature [4]. A broad spectrum of commercial products and applications

contain siloxanes as in cosmetic and hygiene products, car waxes and fuel additives. Eventually, many of these products directly or indirectly reach WWTPs or landfills, and siloxanes are volatilized into biogas. Since the production of sources of siloxanes have been increasing in the last years so has their occurrence in biogases.

Siloxanes are present as trace compounds in biogas at concentrations up to 120 mg m^{-3} [5], particularly octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) are among the most common siloxanes in biogas. Depending on the final use of biogas, upgrading processes will be required prior to the energy conversion system (ECS) [6]. Besides H_2S , siloxane abatement is mandatory in most biogas applications due to the formation of abrasive SiO_2 that originates from the combustion of siloxanes that inhibit heat conduction and lubrication in the conversion engines. Thus, ECS manufacturers strive to limit the concentration of siloxanes up to 0.03 mg mg^{-3} [7] to improve energy applications. Siloxanes concentration are also regulated for gas grid injection, which depends on the national regulations.

The most advanced technique for siloxane abatement is adsorption onto porous materials, specially activated carbons (AC), given the high efficiencies achieved. It is known that activated carbons with higher pore volume show better adsorption capacities

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[8,9]. However, an issue that has been scarcely addressed by the scientific community is the competition between compounds during adsorption, given the fact that most of the published papers report on the adsorption of single pollutants. In previous research [10], the competitive adsorption in activated carbon of siloxanes with other volatile organic compounds (VOC) present in biogas was investigated. From that work it was concluded that the porous features were responsible of VOCs and siloxanes uptake: carbons presenting small-size microporous distribution were more favorable for the adsorption of toluene and limonene whereas carbons that displayed a higher contribution of wider micropores and mesopores were more suitable for siloxane uptake. The phosphoric acid activated carbons showed the largest pore volumes and widths, which led to higher uptakes of siloxanes D4 and D5. However, the reiterated replacement of the carbon bed and its waste disposal are the main drawbacks of this technology which increment the operating expenses (OPEX).

The application of biotechnologies such as biotrickling filtration (BTF) has been widely explored reaching high elimination capacities for many gaseous pollutants [11–14]. Moreover, they have demonstrated to be not only technically and economically convenient but also environmentally friendly [15]. When it comes to biological removal processes, the biodegradation of siloxanes has been distrusted for many years [16], although research on this topic has increased and proved the contrary [17,18,37]. More recently, the use of isolated bacterial species was investigated towards siloxane removal identifying *Methylibium* sp. as a promising siloxane degrader [19]. However, when moving towards siloxane biodegradation in BTFs, mass transfer limitations have been identified as the main challenge to efficiently remove such pollutants [20,21]. The empty bed residence time (EBRT) of the gas in biotrickling filtration is a key parameter to adjust the removal efficiency together with the design of the reactors. In this regard, Santos-Clotas et al. (2019) [22] reported a positive correlation between the removal efficiency of siloxane D5 and the EBRT in a lab-scale anoxic BTF, removing a maximum 37% at 14.5 min of residence time with inert lava rock as packing material. The same BTF was operated at a short EBRT (2 min) with activated carbon as packing media, resulting in a similar performance to that obtained at 14.5 min with lava rock.

In general terms, longer EBRTs tend to enhance the transference of low-soluble gaseous pollutants to the liquid media, therefore higher biodegradation performances are accomplished. Nevertheless, the EBRT is strongly correlated to the reactor size, so increasing this parameter leads to larger bioreactor sizes and space requirements, which entails incremented capital expenses [23].

The possibility of coupling biotrickling filtration with adsorption onto activated carbon has been economically evaluated in the field of odor treatment and compared with other biological technologies as well as their physical/chemical counterparts [24]. Estrada et al. (2012) estimated at $2.7 \text{ € (m}^3/\text{h)}^{-1}$ as the operating costs of an hybrid technology coupling BTF with AC for odor abatement, while the operating costs of AC as the only treatment were almost three times above the costs of the hybrid alternative [25]. It is necessary to note that the removal efficiencies reported for odor abatement in BTFs so far are well above the efficiencies reported for siloxanes in biogas. However, no reports are found in the literature addressing the convenience of coupling technologies for the siloxane issue in biogas valorization.

The objective of the present work is to investigate the feasibility of coupling biotechnologies, particularly BTF, to adsorption onto activated carbon for siloxane abatement in biogas purification. Competitive adsorption of siloxanes with other biogas impurities, and/or partial removal in a BTF will be evaluated in pursuance of decreasing the operational costs associated with the frequent

replacement of exhausted activated carbon and disposal of the spent waste generated.

2. Materials and methods

2.1. Adsorption experiments

2.1.1. Activated carbons

The adsorbents used in this work were commercial activated carbons with different precursor materials and activating agents. The samples were exhaustively characterized in a previous work [10] and the main physical and chemical properties are summarized in Table 1.

2.1.2. Target compounds and gas concentration

Target compounds for adsorption tests were selected based on their occurrence in biogas, including siloxanes and volatile organic compounds. Papadias et al. (2011) set up an exhaustive database of common impurities found in biogas from different sources (i.e. digesters and landfills) reaching three hundred species classified in several categories according to their chemical nature [26]. Among the most characteristic categories hexane was chosen from the class of alkanes, limonene from the cyclic hydrocarbons, toluene from aromatic hydrocarbons, and D4 and D5 as the most representative siloxanes. Their main physicochemical properties are shown in Table 2.

Liquid reagents with purities above 95% for D4, D5, toluene, limonene and hexane were purchased from Sigma Aldrich (USA). All target compounds were placed in a sealed-vial, weighted in an analytical balance (XSR105 Mettler Toledo) and mixed in an orbital shaker at 200 rpm during 1 h to guarantee homogeneity. The generation of a multicomponent test-gas was achieved through a syringe pump (Pump 33, Harvard Apparatus) to infuse the liquid mixture of the target compounds to a N_2 flow of $210 \text{ mL STP min}^{-1}$ set accurately using a mass flow controller (MC Series, Alicat Scientific). The gaseous concentration of each compound was adjusted by the infusion ratio in order to establish four scenarios according to the concentrations reported in Table 3. The concentrations in the test gas were higher than those found in real biogases, shown in Table 2, in order to obtain the breakthrough of the carbon beds in accelerated experimental times, as well as simplified analytical procedures.

The concentration of each compound was continuously measured by a gas chromatograph equipped with a flame ionization detector (GC/FID CP3800, Varian), with a capillary column FactorFour CP8860 (Varian) and a 1-mL loop automatic injection system.

2.1.3. Breakthrough curves

As-received carbon samples were ground and sieved to 212–425 μm of particle size to carry out multicomponent dynamic

Table 1
Main properties and textural characteristics of the ACs.

Material	AC1	AC2	AC3
Precursor material	Anthracite	Coal	Lignocellulose
Activation	Steam	Steam	H_3PO_4
Density [kg m^{-3}]	356	332	340
S_{BET} [$\text{m}^2 \text{g}^{-1}$]	909	1250	1737
V_{T} [$\text{cm}^3 \text{g}^{-1}$] ^a	0.42	0.65	0.91
V_{micro} [$\text{cm}^3 \text{g}^{-1}$] ^b	0.26	0.23	0.29
V_{meso} [$\text{cm}^3 \text{g}^{-1}$] ^c	0.05	0.16	0.25

^a Obtained from N_2 adsorption isotherms at relative pressure P/P_0 0.99.

^b Obtained from applying Dubinin-Radushkevich method to CO_2 adsorption data.

^c Obtained from N_2 adsorption data by applying the 2D-NLDFT-HS model.

Table 2
Physicochemical properties of each compound and average concentrations found in anaerobic digester biogas.

Compound	Molecular formula	Molecular weight [g mol ⁻¹]	Boiling point [°C]	P _{vap} at 25 °C (mm Hg)	Concentration range [mg m ⁻³] ^a
Hexane	C ₆ H ₁₄	86.2	86	153.0	88–381
Toluene	C ₇ H ₈	92.1	111	28.4	4–25
Limonene	C ₁₀ H ₁₆	136.2	179	2.1	54–272
D4	C ₈ H ₂₄ Si ₄ O ₄	296.6	175	1.1	9–244
D5	C ₁₀ H ₃₀ Si ₅ O ₅	370.8	210	0.2	25–275

^a In anaerobic digester biogas reported in Ref. [26].

Table 3
Concentration of each target compound on the test gas for the different scenarios considered.

Compound	Scenario A [mg m ⁻³]	Scenario B [mg m ⁻³]	Scenario C [mg m ⁻³]	Scenario D [mg m ⁻³]
Hexane	2520 ± 41	0	714 ± 27	703 ± 16
Toluene	164 ± 4	0	0	0
Limonene	1713 ± 31	0	0	0
D4	431 ± 15	430 ± 22	377 ± 19	236 ± 11
D5	765 ± 21	765 ± 29	673 ± 25	528 ± 44

adsorption experiments at room temperature (25 ± 2 °C). A mass of 250 mg of AC was packed in a glass fixed-bed column (internal diameter of 7 mm) for each test. Bed heights ranged between 7 and 10 mm depending on the packing density of the material. A schematic of the adsorption experiments is shown in Fig. S1.

Multicomponent dynamic adsorption tests were carried out according to the scenarios described in Table 3 by triplicate. Each adsorption experiment was operated until the compounds' outlet concentration matched the inlet concentration and breakthrough curves were obtained by plotting the C_(t)/C₀ against time. The adsorption capacity of each activated carbon for every target compound (x/M) was calculated following Equation (1);

$$\frac{x}{M} = \frac{Q}{\omega} \left(C_0 t_s - \int_0^{t_s} C_{(t)} dt \right) \quad (1)$$

where x/M is the adsorption capacity for each target compound (mg g⁻¹), C₀ the inlet target concentrations and C_(t) the outlet concentration (mg m⁻³) at a given time, t_s is the bed exhaustion time (s), ω the mass of carbon (g) and Q is the inlet flow (m³ s⁻¹).

In real applications the adsorption capacity is generally reported in terms of adsorbent volume, which considers the quantity of adsorbent that fits the AC vessel. Therefore, for comparing the adsorbent materials regardless the bed size, the bed volume (BV) treated was calculated following Equation (2);

$$BV = \frac{V_W}{V_F} \quad (2)$$

where V_W is the volume of gas treated and V_F the volume of the adsorbent bed. Adsorption capacities and bed volumes treated were calculated until D5 reached 90% breakthrough (i.e. C_(t)/C₀ = 0.9).

2.2. Economic evaluation

A WWTP generating a biogas flowrate of 1000 m³ h⁻¹ containing average concentrations of VOCs (hexane, toluene and limonene) and siloxanes (D4 and D5) was considered as model plant to assess the capital (CAPEX) and operation costs (OPEX) of siloxane removal. Both CAPEX and OPEX calculations were estimated according to the literature revision [24,27]. Capital investments were annualized for a 10-year period to calculate the total annual costs.

In order to estimate the economic data for the adsorption filter in a more realistic scenario, adsorption breakthrough curves were performed for two case-studies at concentrations closer to real biogases. In Case 1 adsorption was the only treatment given to biogas, therefore VOCs and siloxanes were present as in Scenario A though concentration of the target compounds was reduced up to 10 times. Similarly, in Case 2a the concentration of the target pollutants was also reduced except for limonene and toluene that were not present due to its hypothetical removal in a pre-treatment step in a BTF operating at 1.5 min of EBRT. The final concentration for the target pollutants in each case-study for conducting the adsorption tests is described in Table 4.

For the case-study coupling BTF and adsorption onto activated carbons, the volume of the biotrickling filters was calculated following Equation (3) according to the flowrate and EBRT set for Case 2a (1.5 min) and Case 2b (14 min).

$$V = F \times EBRT \quad (3)$$

where V is the reactor volume (m³), F the biogas flowrate (m³ h⁻¹) and EBRT is the empty bed residence time (h). Moreover, the scale-up of a larger bioreactor was calculated following the rule of six-tenths as in Equation (4) [28].

$$C_B = C_A \left(\frac{V_B}{V_A} \right)^\alpha \quad (4)$$

where C refers to the equipment costs (€) and V to the volume of the reactors (m³). α is the scale coefficient, which can vary from 0.3 to 0.9 in a wide range of equipment [28].

For the adsorption filter, the economic data referring to operational costs was estimated taking into account (i) the bed volumes at D4 breakthrough (≥5 mg Si m⁻³) obtained from the breakthrough curves, (ii) the density (in Table 1) and (iii) price of each material. The CAPEX for the adsorption unit was estimated

Table 4
Parameters set for the economic evaluation in the two case-studies.

		Case 1	Case 2a
Impurity concentration [mg m ⁻³]	Hexane	328.7 ± 22.5	135.3 ± 17.2
	Toluene	21.3 ± 1.5	0
	Limonene	177.1 ± 13.2	0
	D4	47.2 ± 4.4	49.7 ± 4.7
	D5	126.2 ± 14.9	94.3 ± 12.3

according to literature [29]. The price for the ACs was established at 2, 4 and 6 € kg⁻¹ for AC1, AC2 and AC3 respectively, according to personal communications with the corresponding manufacturers.

3. Results

3.1. Competitive adsorption

A set of experiments was performed to evaluate the performance of three ACs on the adsorption of cyclic siloxanes D4 and D5 in competition with limonene, toluene and hexane. Breakthrough curves are presented in Fig. 1A depicting the concentration ratio of each compound between the inlet and outlet of the adsorption column ($C_{(t)}/C_0$) along with the experimental time. Solid horizontal lines represent feed concentration, which indicates that the outlet matches the inlet concentration ($C_{(t)} = C_0$) therefore the adsorbent bed is exhausted.

Scenario A (S-A) corresponded to the worst-case scenario where siloxanes and VOCs presented the highest concentrations in comparison with the rest of scenarios (Table 3). In all the carbons tested

(Fig. 1A) the first compound to break through was hexane, showing a steep profile in every case. Even being the highest concentrated compound (2520 mg m⁻³), the low molecular weight and size of hexane (Table 2) made this component the hardest to adsorb. Furthermore, the breakthrough curves showed an overshoot, where the outlet concentration exceeded the inlet concentration ($C_{(t)}/C_0 > 1$). This roll-up effect demonstrated that hexane was weakly adsorbed and even displaced by the other molecules in the mixture that depicted stronger affinities for the adsorbent material.

When it comes to the rest of compounds, the lowest porous-developed AC1 (Fig. 1A-) behaved differently than AC2 and AC3 (Figs. 1A-2 and A-3, respectively); breakthrough of siloxanes as well as toluene and limonene occurred almost simultaneously after 70–80 min of adsorption test. Complete exhaustion of the material (i.e. $C_{(t)}/C_0 = 1$) did not occur after 230 min. Limonene and D5 resulted the most strongly adsorbed compounds displacing both toluene and D4 as shown in competitive breakthrough curves. However, limonene was the last compound to reach its initial concentration though it could not roll the adsorbed D5 out from the porous sites.

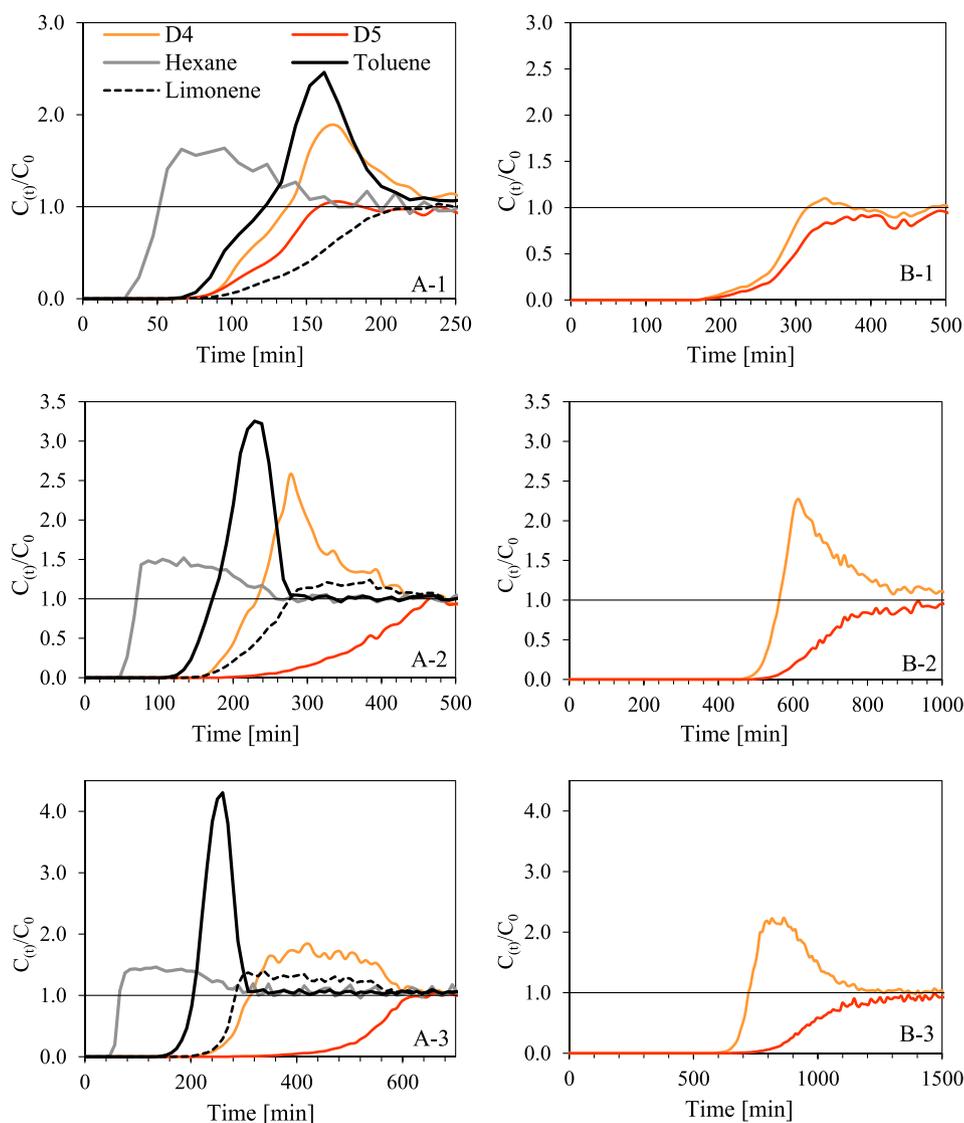


Fig. 1. Breakthrough curves corresponding to scenarios A and B (titled by the letter A and B, respectively) and each activated carbon (denoted by the number after the scenario letter).

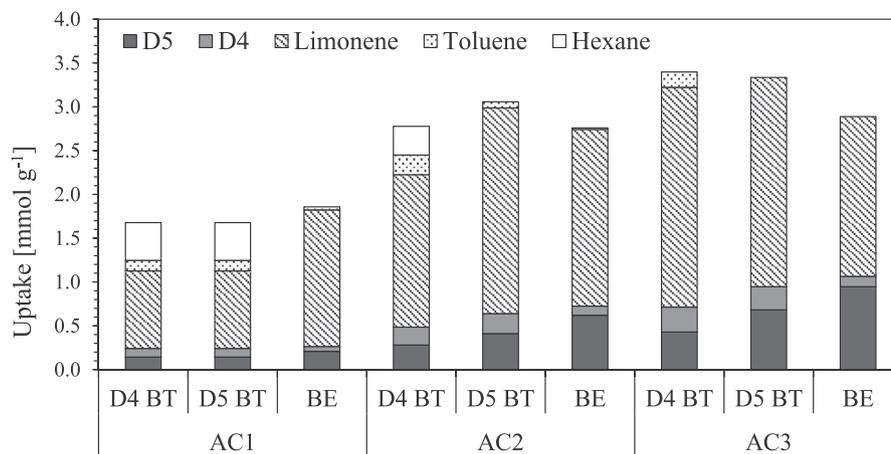


Fig. 2. Distribution of the adsorbed target pollutants in S-A for all materials tested at D4 breakthrough (BT), D5 BT and bed exhaustion (BE).

In the contrary, breakthrough of target compounds in AC2 and AC3 was not simultaneous and followed the order: hexane > toluene > D4 = limonene > D5, being more spaced out in AC3. Pore size distribution of these materials, where mesoporosity contribution is notable, led to higher adsorption of the bulkiest siloxane D5 rolling out the rest of compounds including limonene. Exhaustion of these materials occurred after 480 and 620 min of adsorption test for AC2 and AC3, respectively. Similar competitive behaviors were reported by Cabrera-Codony et al. (2018) who also found strong affinities of siloxane D5 in similar commercial carbons, and correlated its adsorption capacity to the pore volume [10].

The adsorption uptake of each compound was calculated at i) D4 breakthrough (BT), ii) D5 breakthrough, and iii) bed exhaustion (BE). In contemplation of Fig. 2, the amounts of each compound adsorbed at different experimental times is compared. The hexane and toluene remaining at D4 breakthrough were completely rolled out at bed exhaustion for all the carbons tested, while D4 uptake was successively reduced because of the displacement caused by limonene and D5. According to what is observed in the breakthrough curves, limonene was displaced by D5 only in AC2 and AC3 while the amount adsorbed increased until bed exhaustion for AC1. Limonene uptake in AC3 was reduced from 2.5 mmol g⁻¹ at D4 breakthrough to 1.8 mmol g⁻¹ at bed exhaustion, while D5 uptake increased from 0.4 up to 0.9 mmol g⁻¹ at the same time. Thus, AC2 and AC3 are more suitable for siloxane adsorption than AC1 due to the larger pore size development that favored a major adsorption of siloxanes. In order to compare the performance of the activated carbons, the bed volumes were calculated, as it is a parameter frequently used in adsorption applications and indicates the volume of (bio)gas treated per adsorbent bed volume. The bed volumes treated at the time of the first siloxane breakthrough (D4 $C_{(t)}/C_0 = 0.05$) were 23.9 and 35.5 m³ L⁻¹, for AC2 and AC3 respectively (Fig. 3).

In general terms, the odor-causing compound limonene depicted strong affinities with the adsorbent materials indicating high competence for the porosity of ACs. Such competition effect entailed lower adsorption capacities for siloxanes, whose removal from biogas is mandatory for its valorization.

At the opposite side, experiments without VOCs were performed corresponding to scenario B (S-B) to get further insights in the competence of siloxanes for the adsorption sites in each activated carbon (Fig. 1B). Thus, adsorption tests of D4 and D5 in complete absence of VOCs were run to determine the maximum siloxane uptake and the performance decay caused by the presence of VOCs.

A similar competitive behavior was obtained for the three materials regardless the absence of VOCs, although experimental times were remarkably longer than those obtained in S-A. More precisely, a simultaneous breakthrough of D4 and D5 occurred for AC1 after 180 min of adsorption test, which is more than 2 times the breakthrough of siloxanes in S-A. It needs to be highlighted that D4 in this case was not rolled out, which indicates that D4 displacement in S-A was likely caused by limonene. For AC2 and AC3 D5 depicted the strongest affinity displacing D4 from the porous sites. A similar competitive behavior between D4 and D5 was reported by Matsui and Imamura (2010) in activated carbons with S_{BET} ranging 1000–1800 m² g⁻¹ [31]. Bed exhaustion did not happen after ca. 1000 and 1400 min for AC2 and AC3, respectively. The bed volumes of gas treated at D4 breakthrough were much higher than in S-A, reaching 64.8, 139.2 and 186.1 m³ L⁻¹, for AC1, AC2 and AC3, respectively, indicating a five-fold increase in the case of AC3 when comparing both scenarios.

It was observed earlier in S-A that toluene and hexane seemed to have a low impact upon siloxane adsorption, as shown in Fig. 2, given the fact that they were completely displaced at bed exhaustion by the bulkiest siloxane D5 or limonene. In this sense, limonene was expected to significantly influence the performance of the adsorbent beds towards siloxane removal. This fact was also suggested by Papadias et al. (2011) that modelled the adsorption behavior of several VOC mixtures and siloxanes. They reported that terpenes such as limonene were strongly adsorbed in similar activated carbons to the AC1 studied herein. Moreover, increasing their concentration (among other parameters) led to reducing the time for siloxane D4 to break through, thus requiring an earlier bed replacement [26]. The aforementioned authors also noted that hexane could negatively affect siloxane adsorption according to the theoretical models from single-compound adsorption isotherms. In this sense, scenarios C and D (S-C and S-D, respectively) were devoted to assess the influence of siloxane concentration in the feed gas as well as the presence of hexane. For this purpose, toluene and limonene were removed from the feed gas and the concentration of both D4 and D5 was reduced in S-D as indicated in Table 3.

In the adsorption curves of scenario C (Fig. 4C), the profile shape of the compounds was similar to those in S-A, though the absence of limonene in the test gas drastically extended the experimental time in the adsorption tests in comparison with S-A. In terms of bed volumes, this led to an increase in the BV treated for all the adsorbent materials; breakthrough of D4 increased up to 64.5 in

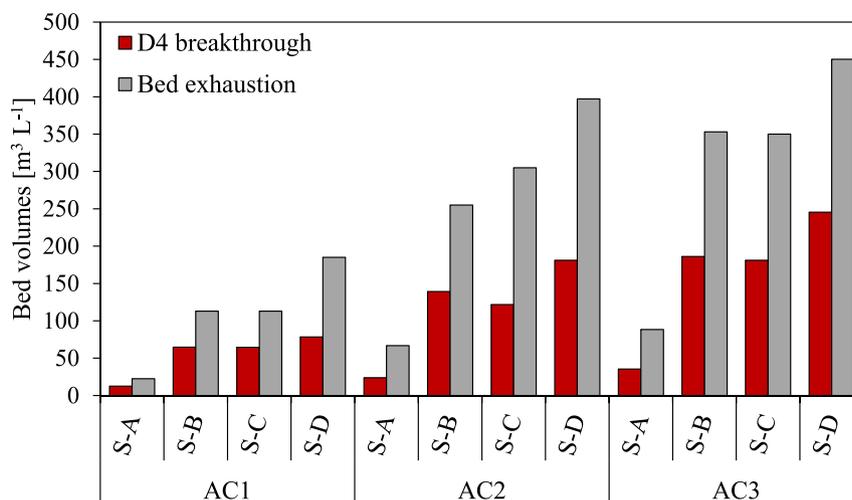


Fig. 3. Bed volumes treated at D4 breakthrough and bed exhaustion for each AC and scenario tested.

AC1, 121.7 in AC2 and 181.1 $\text{m}^3 \text{L}^{-1}$ in AC3 (Fig. 3). Furthermore, without limonene in the inlet gas D5 happened to be the compound with highest affinity in AC2 and AC3 and the responsible for the roll-up phenomena towards D4 and hexane, as expected from the breakthrough curves in S–B. The bed volumes obtained in this scenario did not significantly diverge from those obtained in S–B (with only siloxanes), pointing out that hexane did not much interfere in siloxanes' adsorption. These results are in disagreement with [26] who stated that hexane was the alkane with the greatest effect on the adsorption capacity for D4 according to model predictions.

Finally, S–D represented the scenario with the lowest concentration of siloxanes (236 and 528 mg m^{-3} for D4 and D5, respectively). The curves depicted in Fig. 4D revealed a significant decrease in the slope after the breakthrough because of the adsorption kinetics slow down due to the lower inlet concentration. Thus, the adsorption experiments were further extended up to exceeding the 2000 min in the case of AC3 (Figs. 4D–3) to reach bed exhaustion, which occurred at 450 $\text{m}^3 \text{L}^{-1}$ of BV treated, which was 1.2 and 2.5 times higher than the BV treated in S–C and S–A, respectively. Therefore, decreasing the siloxane concentration entailed longer experimental times, which in practical applications would lead to postponing the media replacement and decreasing the related operational costs.

3.2. Technologies coupling: an economic approach

Adsorption onto AC without biogas pre-polishing is the most common practice in real facilities. The activated carbon denoted as AC1 is currently being used in a WWTP for siloxane removal from sewage biogas, while AC2 and AC3 are commercially available for other applications. Activated carbon is commonly replaced by fresh adsorbent when the carbon material is saturated in a lead-lag configuration.

According to the literature, summarized in Table 5, the three VOCs used in the present study have been efficiently removed through BTFs at short EBRTs [14,32]. However, the abatement of poorly soluble VOCs such as hexane and siloxanes can be hindered due to mass transfer limitations [11,20]. More recently, the co-treatment of VOCs and siloxanes in an anoxic BTF was investigated resulting in a complete abatement of VOCs like toluene and limonene as well as moderate removal efficiencies for siloxanes [22].

In the present study, VOCs like the terpene limonene appeared

to cause a significant impact upon siloxane adsorption by decreasing adsorption capacities towards them and therefore the bed volumes of gas treated were accordingly reduced as well. Nevertheless, biotrickling filtration is a promising technology for gas treatment applications and has been proved capable of eliminating the VOCs herein studied. Thus, the possibility to couple both technologies is suggested as an alternative solution to purify biogas in a more efficient and sustainable way.

In order to evaluate the performance of each activated carbon in more rational conditions, dynamic adsorption experiments were performed by reducing the concentration of the target compounds to values resembling real biogases. In this sense, two case studies were suggested (in Table 4) according to the treatment line followed for biogas purification. The resulting breakthrough curves are shown in Fig. 5A in terms of silicon concentration in the outlet of the column for each AC and both case studies. A concentration of 5 mg Si m^{-3} was considered as a model value within the siloxane tolerance range of different energy conversion systems [6] and was set for calculating the bed volumes and so consider the bed replacement, which is represented in Fig. 5B.

The steam-activated AC1 was the material that depicted the earliest siloxane breakthrough despite the absence of VOCs in Case 2a, where the performance of adsorption was duplicated in comparison with Case 1 (Fig. 5B). On the other hand, AC2 and AC3 demonstrated higher bed volumes (265 and 370 $\text{m}^3 \text{L}^{-1}$, respectively) than AC1 in Case 1 up to a three-fold increase. Moreover, when VOCs were removed in a BTF (Case 2a), specially limonene, the adsorption performance in terms of bed volumes was further increased up to 584 and 690 $\text{m}^3 \text{L}^{-1}$ for AC2 and AC3, respectively.

In contemplation of the adsorption results in both case-studies, a pretreatment of biogas in a BTF for the removal of VOCs, clearly increased the bed volumes treated with all the materials tested. Moreover, if biogas was pretreated and AC3 was used instead of AC1 (AC1 in Case 1 vs AC3 in Case 2a), the durability of the material would be extended up to almost six times. This remarkable lengthening of the material lifespan would induce savings in the operating costs of the adsorption technology, due to a reduced frequency in the replacement of the carbon as well as the exhausted material deposition.

Overall, the competitive trends observed between siloxanes and VOCs in both case-studies followed a similar pattern to the behavior observed in the accelerated adsorption tests with high concentrations (Figs. 1 and 4). However, low concentrated

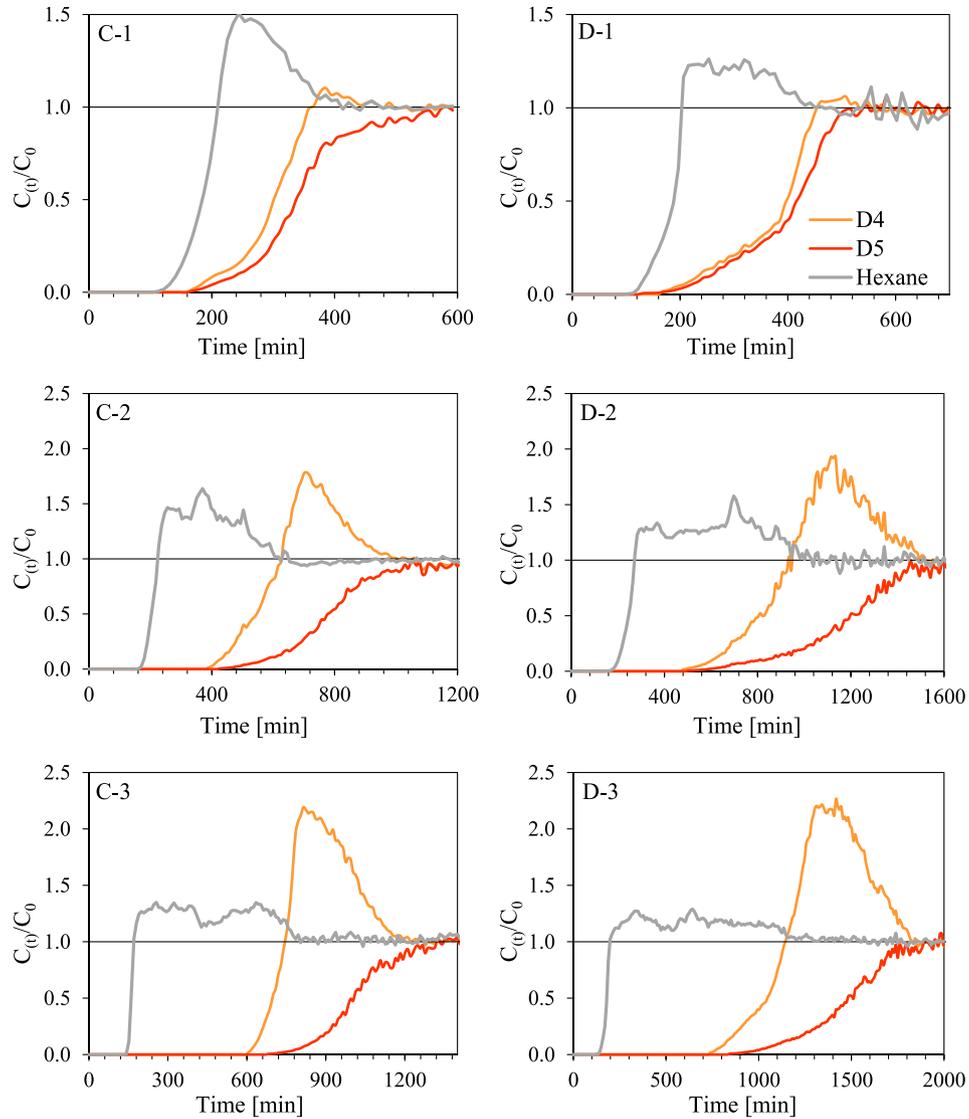


Fig. 4. Breakthrough curves corresponding to scenarios C and D (titled by the letter C and D, respectively) and each activated carbon (denoted by the number after the scenario letter).

Table 5

Literature revision regarding biotrickling filters for the removal of VOCs and siloxanes.

Biotrickling filter operating conditions	Target pollutants	Concentration [mg m ⁻³]	Removal efficiencies [%]	Ref.
Lab-scale aerobic BTF packed with lava rock inoculated with <i>P. aeruginosa</i> . Counter-current. EBRT 3.3–13.2 min	D4	50	48–74	[33]
Lab-scale aerobic and anaerobic BTF packed with cattle bone and lava rock inoculated with activated sludge. Counter-current. EBRT 5–19.5 min	D4	45	10–43	[20]
Lab-scale anoxic BTF packed with lava rock and activated carbon. Inoculum WWTP sludge. Counter-current. EBRT 2–14.5 min	D4	54	15	[34]
	D5	102	45	
	Hexane	375	43	
	Toluene	24	100	
Lab-scale aerobic BTF packed with polyurethane foam cubes and inoculated with WWTP sludge. Counter-current. EBRT 4–43 s	Limonene	220	100	[35]
	Toluene	0.82	>95	
Lab-scale anaerobic BTF packed with lava rock inoculated with WWTP activated sludge. Counter-current.	Hexane	0.75	>80	[32]
	Limonene	8–109	>80	
Lab-scale anoxic BTF packed with Kaldnes rings and inoculated with WWTP sludge. Counter-current. EBRT 1.3–16 min.	Toluene	500	>90	[12]

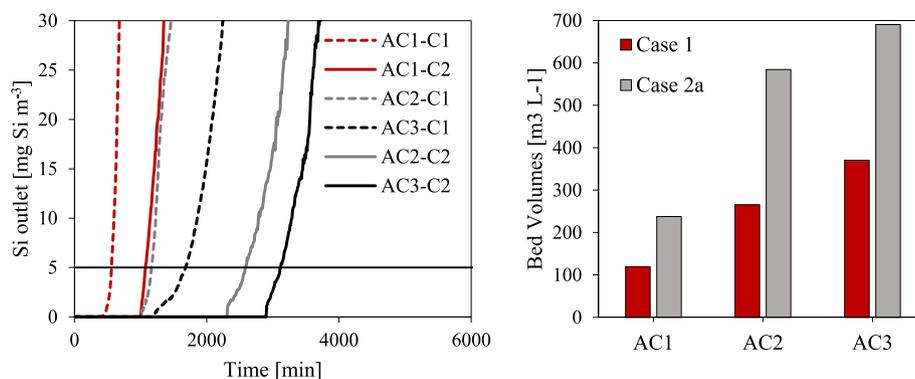


Fig. 5. (A) Breakthrough curves obtained for the activated carbons in Case 1 (C1) and Case 2a (C2), and (B) bed volumes of biogas treated at D4 breakthrough ($>5 \text{ mg Si m}^{-3}$).

adsorption tests were necessary to determine the bed volumes of gas treated for each material so that a proper estimation of the operating costs could be carried out.

A comparative economic evaluation of the operational costs of adsorption using each activated carbon was performed considering the bed volumes treated upon siloxane breakthrough in each case-study, and according to the prices of the materials provided by the suppliers (ranging $2\text{--}6 \text{ € kg}^{-1}$). The steam-activated AC1, which is currently used in the studied WWTP, displayed the highest costs reaching $5.93 \text{ € (1000 m}^3_{\text{treated}})^{-1}$ in case 1. When biological pre-treatment was regarded, in Case 2a, adsorption costs drastically decreased for the three materials. According to their adsorption performance and material price, the lowest operating costs estimated were obtained by the steam-activated AC2 in Case 2a reaching $2.27 \text{ € (1000 m}^3_{\text{treated}})^{-1}$.

The economic feasibility of polishing the biogas in a BTF prior to the adsorption unit was also explored by taking into account not only the operating costs of the carbon filter but also the CAPEX and OPEX of the technologies involved in each case-study (Fig. 6).

Regarding the CAPEX of activated carbon technology, the adsorption unit was considered to be equal for all scenarios at 1400 € year^{-1} , which is within the range of the capital costs of adsorption units published elsewhere [36]. The annual OPEX was calculated according to the costs estimated from the breakthrough

curves, which ranged from $<20000 \text{ € year}^{-1}$ (in Case 2a with AC2) to $>50000 \text{ € year}^{-1}$ (in Case 1 with AC1).

On the other hand, the costs associated with the implementation of a pre-polishing step in a BTF was evaluated in Case 2a. Since the literature points out an incremented siloxane removal efficiency by increasing the EBRT in this type of bioreactors [20,22], the capital costs of this technology were estimated for a BTF operating at a short (1.5 min, Case 2a) and long EBRT (14.5 min, Case 2b). The annual capital costs obtained were ca. 4100 and $15600 \text{ € year}^{-1}$ for Case 2a and Case 2b, respectively, considering a 10-year annualization. A higher residence time in the BTF leads to higher reactor volumes for treating the same flowrate, hence the greater costs obtained in Case 2b. CAPEX of BTF was higher than for the adsorption unit, which is in agreement with other reports [7]. Contrarily to the OPEX of the AC filter, the BTF presented significantly lower operating costs, especially when compared with Case 2b. This remarkable difference is mainly due to the packing material replacement and disposal as a hazardous waste. Activated carbon filters require not only frequent replacement of the saturated material but also its disposal as hazardous waste. In contrast, the packing material in BTFs are much cheaper and have longer lifespans than porous activated carbons.

Overall, the highest total annual costs were obtained in the case-study treating a mixture of siloxanes and VOCs (i.e. Case 1). The

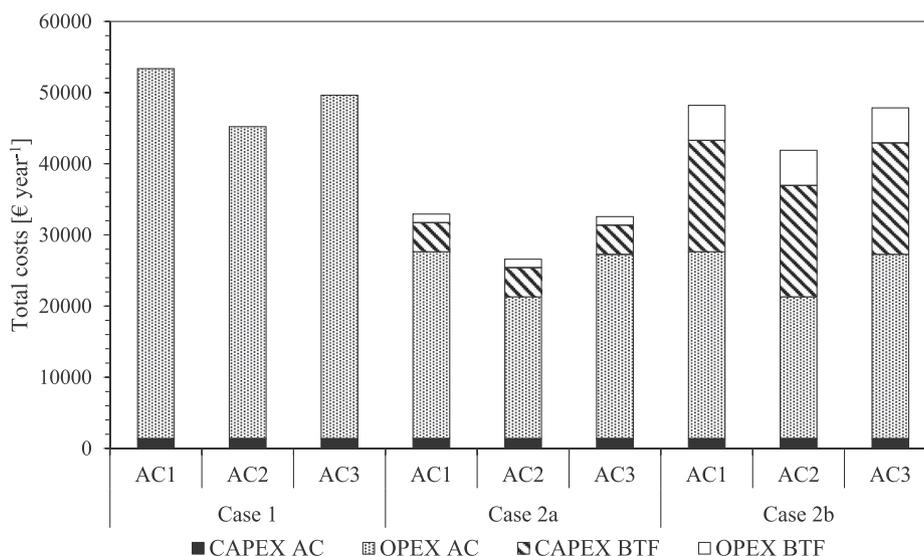


Fig. 6. Total annual costs estimated for the treatment of biogas in the case studies for each activated carbon.

competition of VOCs for the porous sites of the adsorbent material led to reduced BVs and thus more frequent replacement of saturated material, which could be translated into higher operating costs. Even though supplementary costs arise in Case 2a and 2b linked to the pre-treatment of biogas in a BTF, the total annual costs in these case-studies were below the costs in Case 1, specially in Case 2a, suggesting that the implementation of a BTF for polishing biogas from VOCs was economically feasible. Moreover, the lowest annual costs were obtained for the steam AC2 in S–B (26600 € year⁻¹), indicating that Case 2a using such material was the most feasible scenario.

4. Conclusions

The present work investigates the performance of three activated carbons on the adsorption of siloxanes at different concentrations in competence with VOCs aiming to evaluate the beneficial use of biological technologies for biogas purification. In this sense, the absence of terpenes such as limonene in biogas, due to its abatement in a biotrickling filter, led to an extended lifespan of the activated carbon, while using mesoporous carbons reduced the operational costs of the adsorption despite their higher market price.

Moreover, the economic approach on the technologies coupling confirmed the beneficial economic aspect of biotrickling filtration implementation to abate VOCs. The coal-based steam-AC (AC2) resulted in the material depicting the lowest operating costs, which decreased from 5.1 (in Case 1) to 2.3 € (1000 m³_{treated})⁻¹ in the case-study representing a pre-treated biogas in a BTF. Even contemplating both the CAPEX and OPEX of a BTF, the total annual costs were much lower when biogas was pre-polished from VOCs in a BTF than treating biogas entirely in an adsorption filter. Therefore, the installation of a BTF operating at short EBRTs prior to an activated carbon filter with a mesoporous adsorbent, such as AC2, as the adsorbent material would imply savings in the total annual costs by halving them due to the lengthening of the lifespan of the adsorbent as well as a less frequent disposal as hazardous waste.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Eric Santos-Clotas: Investigation, Writing - original draft. **Alba Cabrera-Codony:** Methodology, Visualization, Writing - review & editing. **Maria J. Martín:** Project administration, Funding acquisition, Supervision, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.renene.2020.02.026>.

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