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Article

# Biogas Purification: A Comparison of Adsorption Performance in D4 Siloxane Removal Between Commercial Activated Carbons and Waste Wood-Derived Char Using Isotherm Equations

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**Abstract:** Biogas production from organic waste could be an option to reduce landfill and pollutant emissions into air, water, and soil. These fuels contain several trace compounds that are crucial for highly efficient energy generators or gas injection into the grid. The ability of adsorbents to physically remove such adsorbates was investigated using adsorption isotherms at a constant temperature. We experimentally modelled isotherms for siloxane removal. Siloxanes were considered due to their high impact on energy generators performance even at low concentrations. Octamethylcyclotetrasiloxane was selected as a model compound and was tested using commercially available carbon and char derived from waste materials. The results show that recyclable material can be used in an energy production site and that char must be activated to improve its removal performance. The adsorption capacity is a function of specific surface area and porous volume rather than the elemental composition. The most common adsorption isotherms were employed to find the most appropriate isotherm to estimate the adsorption capacity and to compare the sorbents. The Dubinin-Radushkevich isotherm coupled with the Langmuir isotherm was found to be the best for estimating the adsorption capacity.

**Keywords:** siloxanes; waste materials; biogas; circular economy; adsorption equilibrium isotherms

## 1. Introduction

Biogas production from organic waste could be an option to reduce landfill and emissions into the air, water, and soil. Biogas mainly contains methane (60–70 vol %), carbon dioxide (30–40 vol %), and trace compounds [1]. Among the trace compounds, sulphur and siloxane play an important role in the energy production sector and in injection into gas networks. Biomethane injection into the gas network requires stringent trace compounds limits, fixed by the European authorities (European Standards EN 16723-1 and EN 16723-2). Conversely, energy production can be accomplished with generators based on the Carnot principle or by systems able to directly convert chemical content into electrical energy (solid oxide fuel cell (SOFC) systems). An internal combustion engine can work with a sulphur content in the range of 500 to 1700 ppm(v), and with a 9–44 ppm(v) silicon content [2]. SOFCs are systems with high electrical efficiency with stable behavior at partial load, low noise, and low pollutant emissions [3]. These systems have a stricter limit for trace compounds, especially for sulphur and siloxane compounds, compared with traditional generators due to catalyst deactivation [4–8] and clogging of pores due to silica formation [4,9,10]. Siloxanes, among all trace compounds,

more strongly affect SOFC performance compared with sulphurs and tars [11–14]. Siloxanes are particularly detrimental since they thermally decompose into silicates and micro-crystalline quartz, which cause abrasion to the inner surfaces of combustion engines [15,16], or deposits that interfere with the active surfaces of fuel cell electrodes [17,18]. Siloxanes are widely used in industry due to their properties, including thermal stability, high compressibility, low flammability, and low toxicity. They are not environmentally persistent compounds and generally have low allergenicity [18,19]. They can be found, for instance, in detergents, pharmaceuticals, shampoos, shaving foams, cosmetics, and paper coatings. During the anaerobic digestion of organic waste, these compounds should not be present, unless the collection of waste for recycling is conducted incorrectly [20]. In our previous work, siloxanes were identified in biogas from organic fraction municipal solid waste, especially D3 (hexamethylcyclotrisiloxane), D4 (octamethylcyclotetrasiloxane), D5 (decamethylcyclopentasiloxane), and L4 (decamethyltetrasiloxane) [20]. Within the anaerobic digester, siloxanes can significantly volatilize and end up in the gas phase. Here, the biomass can reach a temperature of around 40 °C, which favors their volatilization. The only possible solution is the complete removal of such compounds [21–26]. To remove siloxane, a physical adsorption approach is more economical and easier than other technical methods such as absorption, cryogenic, and membrane processes [18]. The affordability of physical adsorption is described in previously reported case studies [2,27,28], and its simplicity is related to the low added values of these processes compared with other techniques [2,29].

Physisorption is a mechanism in which the relationships between adsorbent and adsorbate have low interaction strength (van der Waals forces). This low interaction strength is related to the intermolecular forces, which do not involve a significant change in the electronic orbital patterns of the species involved. During physisorption, van der Waals forces regulate the attraction between gas molecules and the porous surface. They have a low heat of adsorption that is only slightly greater than the heat of sublimation of the adsorbate. During chemisorption, a covalent chemical reaction is established between the sorbent site and the organic compound to be removed. A greater heat of adsorption is recorded [30]. High selectivity and a broad concentration range are essential for competitive siloxane adsorption/separation [31]. Several strategies have been developed to improve the adsorption capacity of siloxane. The major issues that influence siloxane removal are: (a) the type of siloxanes considered, e.g., decamethylcyclopentasiloxane (D5) adsorbs better than hexamethyldisiloxane (L2); (b) the humidity of the biogas since water can interact with active pores; and (c) the capacities of the adsorbents used [31]. In summary, the chemical and textural properties of adsorbents are crucial for gas cleaning, starting from the basicity and considering its microporous volume and surface area.

Nam et al. [32] evaluated the adsorption characteristics of siloxanes using commercially available activated carbons and non-carbons, considering L2, D4, and D5. The adsorption characteristics of siloxane are highly dependent on the molecular size of each siloxane and the pores distribution in the adsorbent. Elwell et al. [33] considered the design and analysis of siloxane removal by adsorption from landfill gas. The parameters analyzed included adsorbent type (activated carbon and silica gel), bed height (3.05–9.15 m), inlet siloxane concentration (5–15 mg/m<sup>3</sup>), moisture content (0%–100% relative humidity at STP or RH), and siloxane tolerance limit (0.094–9.4 mg/m<sup>3</sup>). Cabrera-Codony studied 12 commercially available activated carbons (ACs) for the removal of octamethylcyclotetrasiloxane (D4) in dynamic adsorption experiments using different D4 concentrations [34]. Their findings confirmed that the main parameter determining the D4 adsorption capacity is the total pore volume of the AC. Recyclable materials in energy plants show promise for gas cleaning purposes. Some studies considered the use of wastes in a biorefinery concept to produce fuels, power, heat, and value-added chemicals and materials, such as adsorbents. Gutierrez et al. [35] activated biomass wastes (olive and cherry stones) to produce sorbents for the separation of CO<sub>2</sub> from biogas mixtures. Another study showed how ACs, produced by the physical and chemical activation of hydrothermally carbonized biomass (horse manure, grass cuttings, beer waste, and biosludge) have a strong ability to adsorb CO<sub>2</sub> [36].

The removal performance of an adsorbent can be investigated using adsorption isotherm data. Modelling of these experimental data is essential for the comparison and forecasting of adsorption behavior. This last aspect is critical for the evaluation of adsorption capacities and the design of an affordable cleaning system.

In this work, a siloxane compound (D4) was tested with two commercially available ACs and a waste-derived material. The model compound (D4) was selected due to its average concentration level detected in biogas plants [37]. Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin adsorption equilibrium isotherm equations were employed to describe the adsorption of siloxane onto AC.

The main goal of this research was to prove if a waste-derived material can be reused in an energy production plant for gas cleaning purposes. Isotherm equations were employed to estimate the adsorption capacity for siloxane removal.

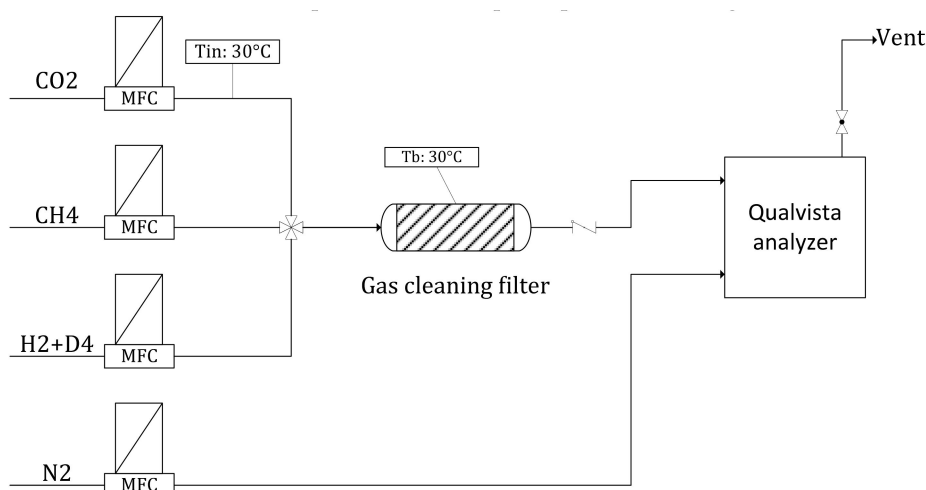
## 2. Experimental Methods

### 2.1. Description of the Experimental Setup

This set-up was used to investigate the siloxane removal, considering D4 as a model compound of the family due to its concentration in a typical biogas mixture (R). Octamethylcyclotetrasiloxane (D4, 20 ppm(v) in H<sub>2</sub>) was prepared and stored in compressed gas bottles (Air Liquide, Collegno, Turin, Italy). The experimental tests were conducted at room temperature with a thermostatic bath (25 ± 0.5 °C) with a simulated biogas flow sent to filter cartridges by mass flow controllers (EL-FLOW, Bronkhorst, Netherlands) with an accuracy of ±2%. The experimental conditions adopted for each sample tested are listed in Table 1. The D4 concentration was increased from 1 to 10 ppm(v), considering 1, 2, 5 and 10 ppm for the tests (named S-01, S-02, S-05, and S-10). The biogas mixture was fixed at CH<sub>4</sub>/CO<sub>2</sub> = 60/35 vol %. Increasing the concentration of D4 from 1 to 10 ppm(v), the carbon dioxide concentration was fixed (35 vol %) and consequently the methane content decreased. This occurred due to technical issues regarding siloxane preparation in compressed bottles. Hydrogen was adopted to contain as much D4 as possible in a stable form at higher pressure. Carbon dioxide was kept constant to avoid interactions with sorbent materials. The hydrogen content does not interact with activated carbon pores. The adsorption capacity of hydrogen is minimal from activated carbons, around 0.01 mg/g [38]. The humidity conditions were not considered because in the real plant application to which the analysis refers, two chiller systems and a silica reactor exist to ensure water-free biogas (the reference site is the one installed in the framework of the European project DEMOSOFC [39,40]). The experimental set-up is represented in Figure 1.

**Table 1.** Experimental conditions adopted for each sample tested: biochar (BIO), C64, and CKC.

Test	S-01	S-02	S-05	S-10
CO <sub>2</sub> (N·mL/min)	175	175	175	175
CH <sub>4</sub> (N·mL/min)	300	275	200	75
H <sub>2</sub> + D4 (N·mL/min)	25	50	125	250
Total flow rate (N·mL/min)	500	500	500	500
CH <sub>4</sub> (%)	60	55	40	15
CO <sub>2</sub> (%)	35	35	35	35
D4 concentrate (ppm(v))	1.0	2.0	5.0	10.0
D4 (mg/m <sup>3</sup> )	4.6	9.2	23.0	45.9



**Figure 1.** Experimental set-up for siloxane isotherm test.

A gas cleaning filter was prepared with PFA (perfluoroalkoxy) tubes and Swagelock fittings (internal diameter (*id*) = 4 mm, L/D (Length/diameter) = 5). PFA material does not interact with siloxanes [29].

The filter was fed with a simulated mixture containing D4 as a pollutant with a gas hourly space velocity of 11.9 kh<sup>-1</sup>. Table 1 lists the experimental conditions adopted, represented in Figure 1.

The sorbent materials used were two commercially available activated carbons: C64 and CKC (Airdep Srl, Verona, Italy) and waste-derived material. CKC is an activated carbon of mineral origin, extruded in 4 mm pellets, thermally activated in an inert atmosphere using steam with 5% potassium bicarbonate (KHCO<sub>3</sub>). It is particularly suitable for the removal of hydrogen sulfide (H<sub>2</sub>S), low molecular weight mercaptans, acid gases, and organic sulfurs. C64 is physically activated using steam flux, and has an alkaline pH on its surface and high porosity. It is suitable for the adsorption of volatile and incondensable compounds, such as siloxanes. The waste-derived material used was biochar. This material was generated, with a small granular shape (~1–2 mm) from the pyrolysis of wood waste by Gruppo RM Impianti Srl (Civitella in Val di Chiana, Arezzo, Italy) in a 200 kW reactor at low temperature (450 ± 10 °C).

## 2.2. Methodology

To maintain the correct aspect ratio (~4) between the pellet and reactor diameter, the sorbents were ground and sieved [41]. A homogenous powder was obtained with a 54–400 μm particle size. The samples were treated using N<sub>2</sub> flow (200 N·mL/min) for 30 min after a pre-treatment at 150 °C with no gas flow for 3 h to remove residual gases inside the pores. After, all samples were flushed with methane and carbon dioxide (clean biogas) for 30 min. D4 concentration was determined at the end of this pre-treatment process. Breakthrough experiments for siloxane removal were performed measuring the breakthrough time. These measurements were repeated twice. More specifically, *t*<sub>0</sub> is the cleaning service time, the period at which the pollutant concentration is zero ppm(v); and *t*<sub>1</sub> is the last detection value, corresponding to 1% of the initial concentration for D4.

The adsorption capacity was calculated in terms of mg/g, according to Equation (1):

$$C_{ads} = \frac{Q_{tot} \times MW \times (t_1 - t_0) \times 0.5}{V_m \times m \times 10^3} \quad (1)$$

where *Q*<sub>tot</sub> is the total gas flow rate (N·L/h); *MW* is the molecular weight of the trace compound removed (g/mol); *C*<sub>in</sub> is the inlet trace compound concentration (ppm(v)); *V*<sub>m</sub> is the molar volume (22.414 N·L/mol); and *m* is the mass of the sorbent (g).

Equation (1) was obtained from the work of Barelli [42]. The area between the breakthrough curve and the saturation line ( $C_{out} = C_{in}$ ) is well approximated by the difference between the rectangle ( $t_1 (h) \times C_{in} (ppm(v))$ ) and the triangle areas ( $0.5 \times (t_1 - t_0)(h) \times 1 (ppm(v))$ ) [42,43].

A biogas measurement system enables the monitoring of siloxane and other biogas components, such as methane, carbon dioxide, oxygen, and hydrogen sulfide (Qualvista Ltd., Helsinki, Finland). This system is based on the NDIR (Nondispersive infrared) method, recorded in approximately 40 min time. The modulated IR (infrared) light source is focused and led through a cuvette. The lens after the cuvette focuses the beam to the gas detector. The information received from the detector enables the system to calculate the total amount of silicon using a specific scientific algorithm (Qualvista Ltd., Helsinki, Finland). The system is sensitive and its detection limit is currently approximately 0.1–0.5 mg Si/m<sup>3</sup> for total siloxane level [44].

### 2.3. Sorbent Characterization: SEM/EDS

The sorbent materials adopted were characterised in terms of their composition, surface area, micropore volume, and morphology structure. The elemental composition measurements were recorded by scanning electron microscopy (SEM; FEI Inspect, Philips 525 M, Hillsboro, OR, United States) coupled with EDS (Energy Dispersive X-ray Spectrometry) analysis (SW9100 EDAX, FEI Inspect, Philips 525 M, Hillsboro, OR, United States). The qualitative results are reported in Table 2.

**Table 2.** Composition in terms of weight fraction for the materials tested.

Element	Biochar	C64 (Airdep, Verona, Italy)	CKC (Airdep, Verona, Italy)
C	99.5	81.89	80.83
O	-	13.47	14.04
Si	-	0.99	1.03
Al	-	0.80	0.79
K	0.24	0.74	1.05
Ca	0.28	0.76	0.89
Fe	-	0.74	0.81
S	-	0.30	0.38
Mg	-	0.17	0.16
Na	-	0.14	-

The adsorption isotherms for N<sub>2</sub> at 77 K were determined using a Quantachrome Autosorb 1 (Boynton Beach, FL, USA). The samples were outgassed at 423 K overnight before the adsorption measurements. The experimental equipment allows the measurement of the relative pressure until 10<sup>-6</sup> bar. The specific surface areas were calculated using the Langmuir equation in the relative pressure range of 0.04 to 0.1 bar. The micropore volumes were determined using the t-plot method in the relative pressure range of 0.15 to 0.3 bar. For the carbon-based materials, the pore size was evaluated using the density functional theory (DFT) method, using the NLDFT (Non Localized Density Functional Theory) equilibrium model for slit/cylindrical pores [45] (Table 3). However, traditional DFT fails to describe long-range effects accurately. Electrostatic effects and the Notably, all measurements were assessed with the same procedure and relative measures are in accordance with each other.

**Table 3.** Surface and volume (V) characteristics for the materials tested.

Variable	Unit	Biochar	C64 (Airdep, Italy)	CKC (Airdep, Italy)
Specific surface area	(m <sup>2</sup> /g)	75.3	796.8	663.5
V microporous (<2 nm)	(cm <sup>3</sup> /g)	0.02	0.29	0.22
V mesoporous (2–45 nm)	(cm <sup>3</sup> /g)	0.02	0.066	0.187
Total pore volume	(cm <sup>3</sup> /g)	0.04	0.358	0.408

The most abundant element in the biochar sample was carbon followed by calcium and potassium. C64 and CKC had similar carbon contents with similar elemental composition, but different structures, specific surface areas, and micropore volumes (Table 3).

The concentrations of K and Ca are important for sulphur compound removal, as reported by Tepper and Richardson et al. [46,47]. Transition metals are also important for salt formation with trace compounds.

The isotherm graphs recorded, according to IUPAC (International Union of Pure and Applied Chemistry) classification, are type I, typical of microporous materials, with a sharp increase in adsorbed volume at low relative pressures due to the capillary condensation of the adsorbate inside the micropores. At higher relative pressure, the presence of a hysteresis loop was observed, and its shape suggests the presence of slit porosities due to the aggregation of the primary particles.

### 3. Results and Discussion

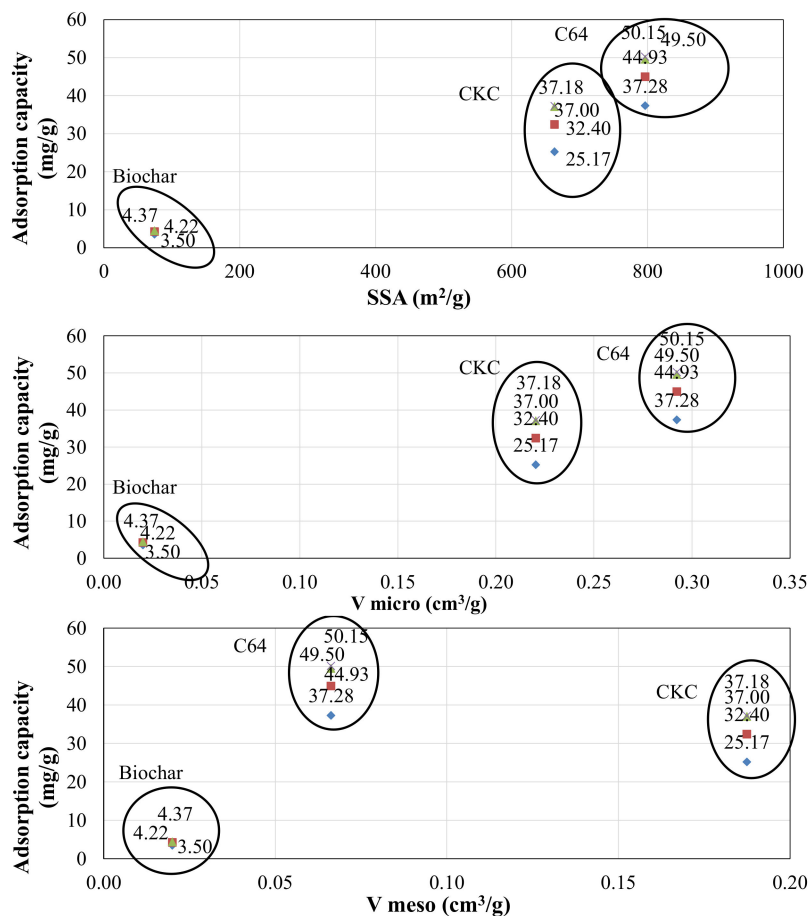
#### 3.1. Adsorption Capacity Related to Physical Sorbent Characteristics

The physical parameters deduced by nitrogen adsorption/desorption measurements are reported in Table 3. These parameters are related to the adsorption capacity of D4. Figure 2 compares the adsorption capacity of D4 considering the specific surface area and the microporous and mesoporous volumes of the sorbents used. Biochar and commercial carbons were compared. The adsorption capacity is a function of the specific surface area and pores volume. As reported previously [21,48], a larger specific surface area implies better adsorption capacity of the pollutant to be removed. In addition to this information mainly related to sulphur compound removal, in this study, micropore and mesopore volumes were also observed to be positively related with the removal of D4. The microporous volume for ACs is one order of magnitude higher than biochar (Table 3). This produces an adsorption capacity one order of magnitude higher than that of biochar. D4 has an average molecular diameter around 1 nm [48], showing how biochar can barely remove this molecule without any pre-treatment. The adsorption capacity for the removal of 4.59 mg/m<sup>3</sup> of silicon compound (D4) is 3.5 mg/g. This suggests that biochar must be activated, at least with physical methods, heated with an active agent, such as steam or carbon dioxide, to improve their physical properties, mainly microporous and mesoporous volumes and specific surface area.

The best activated carbon performance was recorded for C64 instead of CKC. The adsorption capacity for the removal of 4.59 mg/m<sup>3</sup> (D4) is 25.2 mg/g for CKC and 37.3 mg/g for C64. Compared with CKC, C64 has a similar elemental composition but different physical structure. C64 shows a specific surface area 17% higher than CKC. The microporous volume for C64 is 24% higher than that of CKC. These results show how physical properties are important for the removal of siloxanes. Another important factor is related to the activation method. In this work, both materials were activated by steam at high temperature with alkaline salts. Wider micropores (1–2 nm) and narrow mesopores (<2.5 nm) in the activated carbon play an important role in the removal of D4 [21]. The difference in D4 adsorption capacity between C64 and CKC can be attributed to their difference in the number of such pores. C64 has a higher micropores content, whereas CKC has a higher mesopores content. This size of pores is not small enough to retain D4 from the biogas mixture.

#### 3.2. Adsorption Isotherms and Experimental Modelling

Adsorption isotherms are universally recognized for comparing and predicting the performance of sorbent materials. In this study, several popular isotherm equations were considered (Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin). Other isotherm equations can be found in the literature [49]. Sips' equation is an extension of the Freundlich equation; it has a finite limit at sufficiently high pressure (or fluid concentration). Toth and Unilan equations were used to describe the adsorption of hydrocarbons and carbon oxides on activated carbon and zeolite. Another equation, proposed by Keller et al. (1996) has a similar form to Toth's equation [50].



**Figure 2.** Adsorption capacity values in relation with specific surface area (SSA), and microporous (micro) and mesoporous (meso) volumes. (x 10 ppm(v); Δ 5 ppm(v); □ 2 ppm(v); ◇ 1 ppm(v)).

### 3.2.1. Langmuir Isotherm

Langmuir isotherm is an empirical equation that assumes adsorption can only occur on a monolayer of the outer surface of the adsorbent. The sites, located on the outer surface, are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules [51]. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The non-linear expression of Langmuir isotherm is illustrated in the Equation (2). Langmuir adsorption parameters were determined by transforming the Langmuir equation into a linear form using Equation (3).

$$q = \frac{q_m K_L C}{1 + K_L C} \quad (2)$$

$$\frac{C}{q} = \frac{1}{q_m} C + \frac{1}{q_m K_L} \quad (3)$$

where  $C$  is the equilibrium concentration of siloxane ( $\text{mg}/\text{m}^3$ ),  $q$  is the amount adsorbed of siloxane in the adsorbed phase ( $\text{mg}/\text{g}$ ),  $q_m$  is the maximum loading capacity of siloxane at saturation corresponding to a complete monolayer coverage ( $\text{mg}/\text{g}$ ), and  $K_L$  is the adsorption affinity constant function on the heat of adsorption ( $\text{m}^3/\text{mg}$ ).

The adsorption capacity for the removal of D4 increases with the concentration value that must be removed, as depicted in Figure 3 and Table 4. Langmuir isotherm allows simulating the adsorption capacity obtained experimentally with a limited relative error. The maximum percentage error to remove  $2.3 \text{ mg}/\text{m}^3$  (Si) for biochar is 6.9%, 4.5% to remove  $4.59 \text{ mg}/\text{m}^3$  for C64, and 7.1% for CKC.



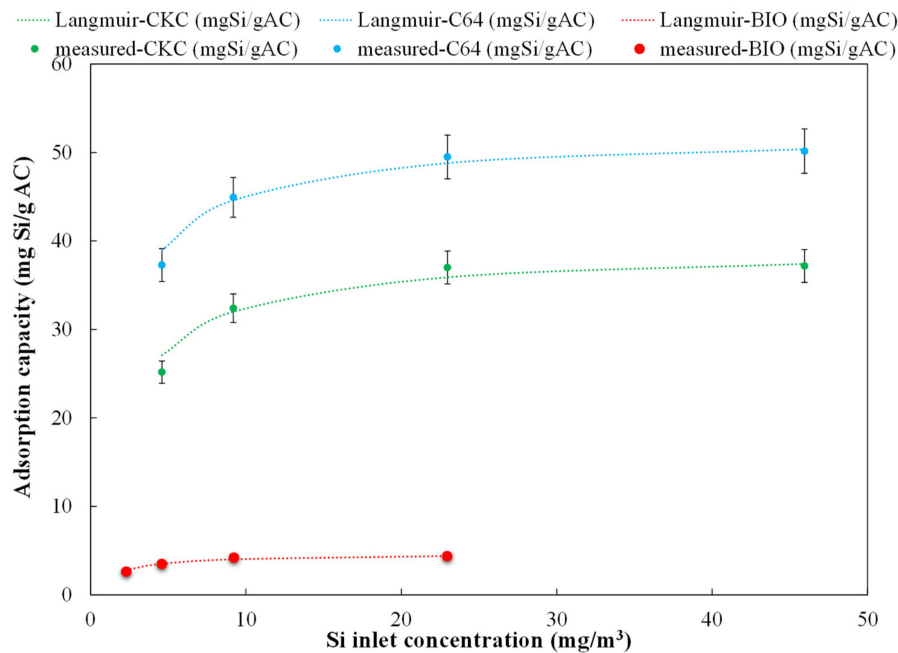


Figure 3. Langmuir isotherm for D4 removal with biochar, C64 and CKC. AC, activated carbon.

Table 4. Adsorption capacity estimated with isotherms for D4.

	Si (mg/m <sup>3</sup> )	q <sub>measured</sub> (mg/g)	Langmuir q <sub>calculated</sub> (mg/g)	Error (%)	Freundlich q <sub>calculated</sub> (mg/g)	Error (%)	DR q <sub>calculated</sub> (mg/g)	Error (%)	Temkin q <sub>calculated</sub> (mg/g)	Error (%)
Biochar	2.3	2.64	2.83	6.89	2.84	7.34	2.64	0.12	2.85	7.5
	4.59	3.5	3.53	0.79	3.3	5.86	3.5	0.9	3.38	3.73
	9.19	4.2	4.03	4.77	3.85	9.64	4.1	3.17	3.9	8.1
	22.97	4.37	4.4	0.64	4.7	6.98	4.47	2.08	4.60	4.96
C64	4.59	37.28	39.03	4.47	39.08	4.59	37.5	0.6	39.13	4.7
	9.19	44.93	44.62	0.7	42.63	5.4	44.4	1.19	42.94	4.63
	22.97	49.5	48.82	1.4	47.83	3.49	49.13	0.75	47.99	3.15
	45.94	50.15	50.4	0.48	52.18	3.88	50.82	1.3	51.8	3.19
CKC	4.59	25.17	27.12	7.17	26.88	6.36	25.4	0.97	26.97	6.65
	9.19	32.4	32	1.2	30.16	7.4	31.82	1.8	30.56	6
	22.97	37	35.90	3.07	35.1	5.37	36.4	1.6	35.32	4.77
	45.94	37.18	37.4	0.6	39.40	5.63	38.09	2.39	38.9	4.45

To evaluate the Langmuir isotherm's ability to describe the adsorption capacity decrease, a dimensionless constant is considered. This constant determines the suitability of different types of the isotherm. It is commonly known as a separation factor ( $R_L$ ) and was defined by Weber and Chakravorti [52] as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where  $K_L$  (m<sup>3</sup>/mg) is the Langmuir constant and  $C_0$  is the adsorbate initial concentration (mg/m<sup>3</sup>). In this context,  $R_L$  indicates the adsorption nature to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ).

As the separation factors decrease, the concentration of D4 to be removed for all the sorbents increases. Biochar starts with an  $R_L$  value around 0.28 (2.3 mg/m<sup>3</sup>) and ends at 0.06 (23 mg/m<sup>3</sup>). The same trend was recorded for C64 and CKC. The  $R_L$  decreased from 0.2 to 0.03 for the first activated carbon, decreasing from 0.23 to 0.04 for CKC. These values are far from linear for an adsorbent, so they prove the favorable nature of the adsorption using carbon-based materials. The Langmuir isotherm can be adopted to estimate the adsorption capacity for the sorbents considered with a relative error around 3% for biochar and CKC, and a relative error around 1.7% for C64. This equation is one of the

best for estimating the adsorption capacity of Si molecules for carbon-based materials, as reported previously [32].

### 3.2.2. Freundlich Isotherm

The Freundlich isotherm is the earliest known relationship describing non-ideal and reversible adsorption. This equation can be applied to describe the adsorption characteristics of heterogeneous surfaces [53]. The non-linear expression of Freundlich isotherm is provided in Equation (5) and the linear form in Equation (6).

$$q = Kf(C)^{1/n} \quad (5)$$

$$\ln q = \ln Kf + 1/n \times \ln C \quad (6)$$

where  $C$  is the equilibrium concentration of siloxane ( $\text{mg}/\text{m}^3$ ),  $q$  is the amount adsorbed of siloxane in the adsorbed phase ( $\text{mg}/\text{g}$ ),  $n$  is the adsorption intensity, and  $K_{ef}$  is the Freundlich isotherm constant ( $\text{mg}/\text{g}$ ).

The adsorption capacity estimated with the Freundlich isotherm shows a maximum relative error higher than the Langmuir isotherm (Figure 4 and Table 4). For biochar, this value is around 9.6% at  $9.19 \text{ mg}/\text{m}^3$  of Si, but lower for C64 (5.4%) and CKC (7.4%). The degree of heterogeneity can be determined from the magnitude of  $1/n$ . When  $1/n$  is close to 0, the degrees of heterogeneity and adsorption capacity increase [32,54]. In this study, the lowest value of  $1/n$  (0.13), or the highest degree of heterogeneity and the increase in adsorption capacity, was recorded for C64. This behavior was confirmed using experimental values of adsorption capacity. CKC has a  $1/n$  value higher than C64, confirming a lower adsorption capacity. The highest  $1/n$  value (0.22) was recorded for biochar. This confirms the lower heterogeneity strength and adsorption capacity of biochar. Despite this information about the strength of the adsorption capacity for sorbents material, Freundlich isotherm is the least appropriate equation for estimating the adsorption capacity of Si molecules with carbon-based materials. In Nam et al., the Freundlich isotherm was also the worst isotherm for estimating the adsorption capacity for D4 and L2 [32].

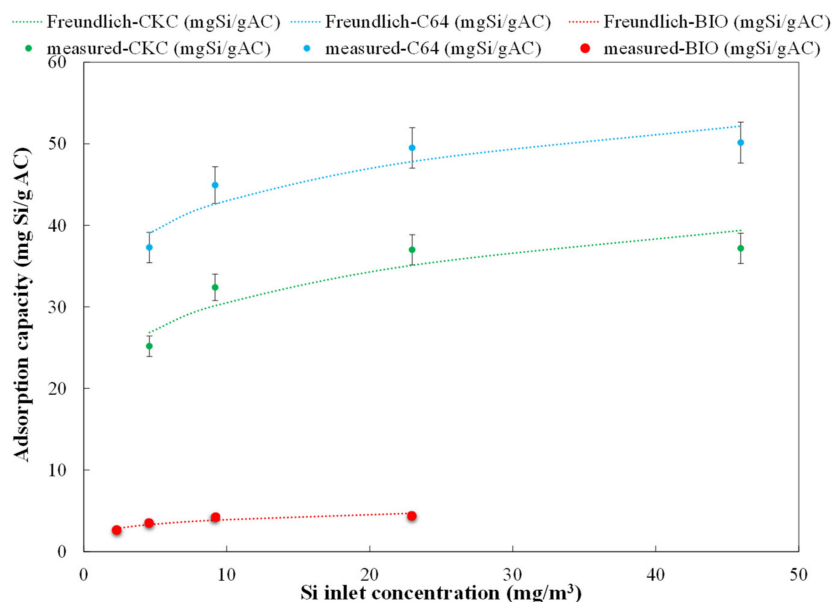


Figure 4. Freundlich isotherm for D4 removal with biochar, C64, and CKC.

### 3.2.3. Dubinin-Radushkevich Isotherm

The Dubinin-Radushkevich isotherm (DR) is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogenous surface [54]. The non-linear isotherm is provided in Equation (7), with the linear in Equation (8).

$$q = q_s \exp(-KDe^2) \quad (7)$$

$$\ln q = \ln q_s - KDe^2 \quad (8)$$

where  $C$  is the equilibrium concentration of siloxane ( $\text{mg}/\text{m}^3$ ),  $q$  is the amount adsorbed of siloxane in the adsorbed phase ( $\text{mg}/\text{g}$ ),  $q_s$  is the theoretical isotherm saturation capacity ( $\text{mg}/\text{g}$ ),  $KD$  is the Dubinin-Radushkevich isotherm constant related to the mean free energy adsorption ( $\text{mol}^2/\text{kJ}^2$ ), and  $e$  is a parameter evaluated as  $e = RT \ln\left(1 + \frac{1}{C}\right)$ , where  $R$  is the gas constant ( $\text{J}/\text{mol}\cdot\text{K}$ ) and  $T$  is the absolute temperature (K).

The adsorption capacity estimated with the Dubinin-Radushkevich isotherm has the lowest relative error values for C64, as shown in Figure 5. The maximum relative error was recorded for biochar (3.2%). These errors are below 2% for C64 and below 2.5% for CKC (Table 4). This equation coupled with the Langmuir equation is the best isotherm for estimating the adsorption capacity of Si molecules with carbon-based materials.

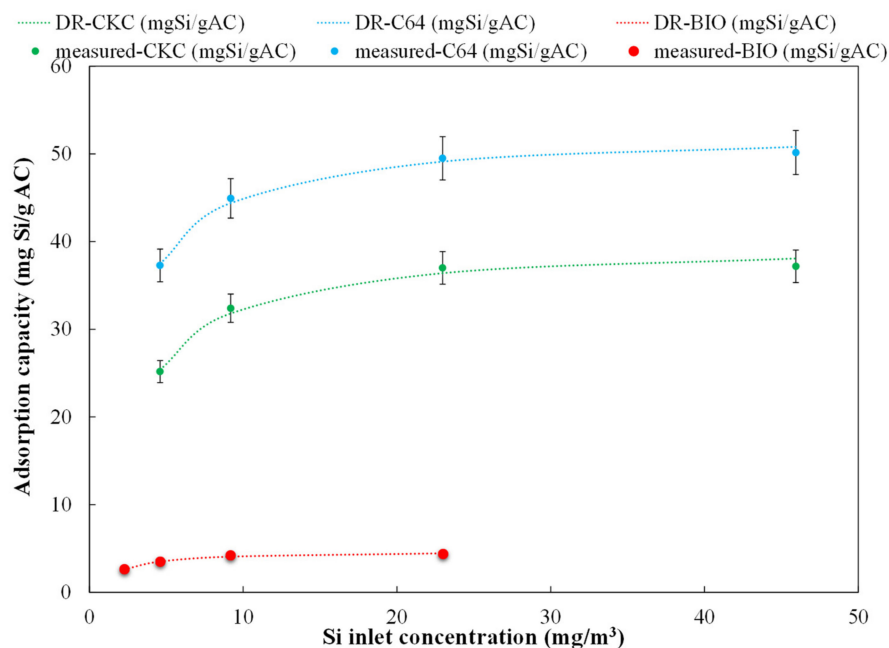


Figure 5. Dubinin-Radushkevich isotherm for D4 removal with biochar, C64 and CKC.

### 3.2.4. Temkin Isotherm

The Temkin isotherm assumes that the heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmically with coverage [55]. The non-linear isotherm is provided in Equation (9), while the linear in Equation (10).

$$q = \frac{RT}{b} \ln(AtC) \quad (9)$$

$$q = B \ln A_t + B \ln C \quad (10)$$

where  $C$  is equilibrium concentration of siloxane ( $\text{mg}/\text{m}^3$ ),  $q$  is the amount adsorbed of siloxane in the adsorbed phase ( $\text{mg}/\text{g}$ ),  $A_t$  is the Temkin isotherm equilibrium binding constant ( $\text{m}^3/\text{g}$ ),  $B$  is a constant

related to the heat of sorption (J/mol),  $R$  is the universal gas constant (J/mol·K),  $T$  is the absolute temperature (K), and  $b$  is the Temkin isotherm constant.

Figure 6 and Table 4 describe the adsorption capacity behavior estimated using the Temkin isotherm. This equation shows higher relative errors, especially at lower Si concentration values due to the logarithmic trend of the molecules coverage of the available sites. This is the third equation we used to estimate the adsorption capacity for the sorbents investigated.

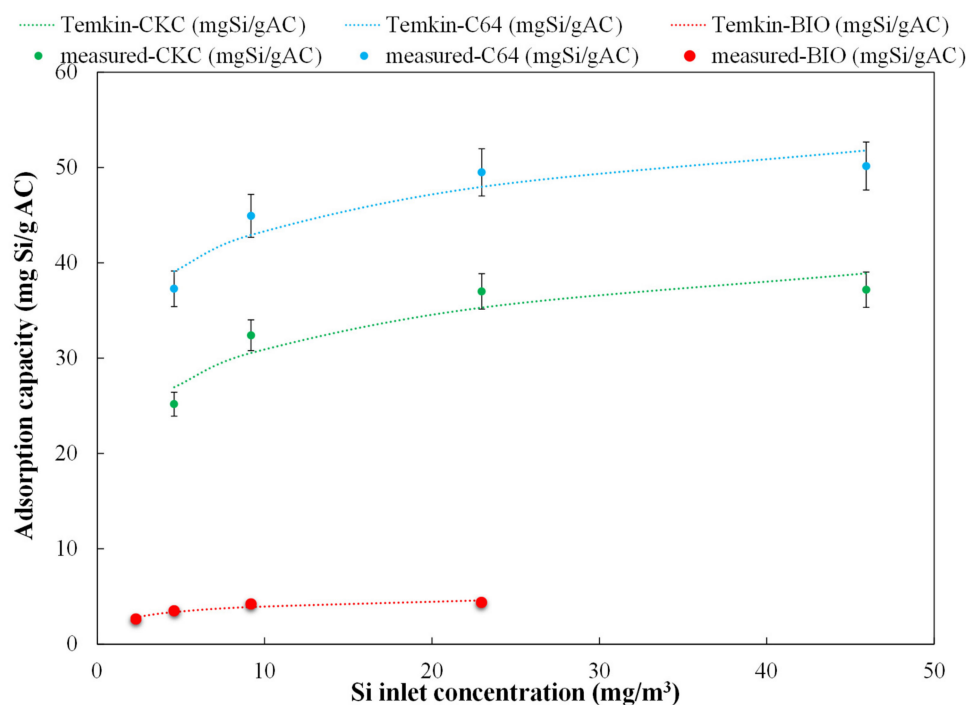


Figure 6. Temkin isotherm for D4 removal with biochar, C64, and CKC.

#### 4. Conclusions

In this study, we experimentally modelled adsorption isotherms for siloxane removal using commercial and waste-derived materials. A siloxane compound (D4), contained in biogas produced from organic waste, was tested. Recyclable materials in energy plants are considered promising for gas cleaning purposes. Waste-derived materials, such as biochar from wood pyrolysis with no activation processes, show lower adsorption capacities than commercially available AC to remove D4. These results suggest that biochar must be activated, at least with physical methods, in heat with an active agent, such as steam or carbon dioxide, to improve their physical properties so that they are comparable to commercially available materials. This will require future research. The adsorption capacity is a function of specific surface area and pores volume rather than the elemental composition. A larger specific surface area implies better adsorption capacity. In this study, micropore and mesopore volumes were also observed to be positively related with the removal of D4.

Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption equilibrium isotherm equations were considered and the relative errors from measured values were reported and discussed. The degree of heterogeneity can be determined from the magnitude of  $1/n$  from the Freundlich isotherm. In this study, the lowest  $1/n$  (0.13) or the highest degree of heterogeneity and the increase in adsorption capacity was recorded for C64. This behavior confirmed the higher removal ability of C64. The adsorption capacity estimated with the Dubinin–Radushkevich and the Langmuir isotherms showed the lowest relative error values. The maximum relative error was recorded for biochar (3.2 and 3%). These errors were below 2% for C64 and around 2.5% for CKC. Dubinin recorded Radushkevich and the Langmuir isotherm were the best equations for estimating the adsorption capacity of Si molecules with carbon-based materials.

Future studies will focus on a pilot plant experimental testing using the results achieved from this work at the DEMOSOFC plant. Biochar can be adopted as a first abatement reactor for siloxane removal, helping to prolong the service life of ACs.

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## Nomenclature

$C_{in}$	Inlet trace compound concentration (ppm(v))
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
DFT	Density functional theory
EDS	Energy dispersive x-ray spectrometry
GHSV	Gas hourly space velocity ( $h^{-1}$ )
$I_d$	Internal diameter
IR	Infrared light source
L/D	Length/Diameter ratio
L4	Decamethyltetrasiloxane
M	Mass of sorbent (g)
MFC	Mass Flow Controller
MW	Molecular weight of the trace compound removed (g/mol)
NDIR	Nondispersive infrared sensor
NLDFT	Non-localized density functional theory
OFMSW	Organic fraction of municipal solid waste
PDMS	Polymeric dimethylsiloxane membrane
PFA	Perfluoroalkoxy alkane polymers
ppb(v)	Parts per billion by volume
ppm(v)	Parts per million by volume
$q_{measured}$	Amount of siloxane adsorbed (mg/g)
$Q_{tot}$	Total gas flow rate (N·L/h)
RH	Relative Humidity
SEM	Scanning electron microscopy
SOFC	Solid oxide fuel cell
SSA	Specific surface area ( $m^2/g$ )
STP	Standard Temperature and Pressure
$T_b$	Bulk Temperature of gas cleaning filter
$V_m$	Molar volume (22.414 N·L/mol)
$V_{meso}$	Mesoporous volume ( $cm^3/g$ ): 2–50 nm
$V_{micro}$	Microporous volume ( $cm^3/g$ ): <2 nm
VOCs	Volatile organic compounds

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