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Adsorption of linear and cyclic siloxanes on activated carbons for biogas purification: sorbents regenerability

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Abstract

Two commercial activated carbons, namely STIX and AP4, were selected to investigate their ability for siloxane adsorption and further thermal regeneration in relation with their different physico-chemical properties. In the frame of biogas purification, the studied siloxanes were L2, L3, L4 (linear molecules) and D4, D5 (cyclic molecules). The maximum capacity of adsorption was estimated by gas chromatography and gravimetric methods. AP4 presents better adsorptive properties comparing with STIX irrespective of the type of siloxane. Thermal regeneration after siloxanes adsorption was followed up to 400  C by both gas chromatography and in situ DRIFTS. Except L2, the siloxane polymerization proceeds on the AC containing alkali metals (K, Na) as revealed by the observed release of their decomposition products during the thermodesorption treatment. The same sites are responsible for the cleavage of Si-O bonds in linear molecules and formation of L2 as primary product above 100  C. The presence of such sites, possibly strong basic sites, is detrimental to

the regenerability of the spent adsorbent and to the adsorption which could be limited by partial blockage of the AC porosity. Interestingly the regenerability of the alkali-free AC depends only on the volatility of the siloxane.

Keywords: siloxane adsorption, activated carbons, linear and cyclic siloxanes, biogas purification

1. Introduction

Concerns on the climate change and the depletion of the available oil and gas reserves prompted a broad discussion on the using of biogas as a clean renewable energy resource. Biogas is usually produced by anaerobic digestion of organic matters in landfills and waste water treatment plants, containing mostly of CH₄ (45 – 70%), CO₂ (25 – 40%) and N₂ (1 – 17%) [1]. Thanks to its high methane content, biogas can substitute natural gas in many applications such as heat and electricity generation for household and industry, bio-fuel for vehicle and injection into gas grid [2]. However, a wide variety of trace adverse compounds (sulfur and halogen containing compounds, NH₃, siloxanes,...) in biogas hampers its large application [3]. In recent years, a special attention was paid to the presence of siloxanes impurities due to their negative impact on the biogas process equipment (e.g. turbines, engine parts, fuel cells and catalysts). Indeed the abrasive silica, the decomposition product of siloxanes, can accumulate up to several millimeters on the surface of pistons, cylinder heads, gas turbines, internal combustion engines and other components inducing the premature failures of biogas upgrading equipments [4-8]. Produced by the degradation and/or volatilization of organosilicons added to consumer products, such as detergents, shampoos, cosmetics, paper coatings textiles etc. [9], the siloxanes are linear (L) and cyclic (D)

compounds containing $-\text{Si}(\text{CH}_3)_2-\text{O}-$ functional groups. Depending on the number of silicon atoms in the molecule, the most common siloxanes in biogas are hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5), hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6).

Table 1. Concentration of siloxanes (in mg m^{-3}) in various biogas [10–12]

Biogas type*	L2	L3	L4	D3	D4	D5	References
LFG	0.38 - 1.31	0.03 - 0.05	<0.01	0.01 - 0.45	4.24 - 8.84	0.40 - 1.09	[10]
LFG	0 - 0.22	0 - 0.05	0 - 2.30	0.60 - 2.29	0.21 - 4.30	0.60 - 1.31	[11]
WWTP	0.01 - 0.05	0.02 - 0.03	0.02 - 0.15	0.14 - 0.20	2.87 - 6.98	7.75 - 9.65	[10]
WWTP	0 - 0.09	0.03 - 0.2	0.51 - 1.29	0 - 0.06	0.10 - 1.21	0.90 - 27.05	[11]
WWTP	0 - 0.03	0.03	0 - 0.08	0.33 - 0.74	2.91 - 4.12	38.85 - 45.80	[12]

*WWTP: Waste Water Treatment Plant, LFG: Landfill Gas

Table 1 shows the concentration of various siloxanes measured in biogas issued of different landfills or wastewater treatment plants [10-12]. As it can be seen, D4 and D5 are the most abundant siloxanes in biogas while L2, L3, L4 and D3 are present generally at trace level.

The upper limit of the total siloxane concentration in biogas, as specified by engine manufacturers, must be in the range of 0.03 to 28 mg m^{-3} [4]. To satisfy such requirements, the siloxanes removal from biogas is necessary. Currently, adsorption on activated carbon (AC) is the most widely used method due to its low cost and high performances [13]. Textural properties such as specific surface area and porosity were determined as the most important parameters affecting the adsorption capacity of ACs [14-16].

The main drawback of the technology is the only partial regeneration of ACs after siloxanes adsorption, inducing the increase of the operating cost [17]. However, several works reporting efficiency tests for different siloxane removal systems (e.g. activated carbon, silica gel, molecular sieves) have suggested that the ACs remain the choice materials for biogas purification from siloxanes [18,19]. For instance, the investigations of Montanari et al. [18] on D3 removal from biogas showed that inorganic materials such as silica and NaX zeolite are not only less efficient than pure ACs in the adsorption step but show similar difficulties in the regeneration one. Matsui and Imamura [14] investigated the D4 removal performances of many kinds of commercial activated carbons together with 13X and 8A molecular sieves and silica gel. Although the authors did not address the regeneration issue, they found that the selected activated carbons had considerably higher ability for D4 adsorption than the silica gel and molecular sieves. Similar results were found by Ortega and Subrenat [20] when using as adsorbents for L2 and D4 two activated carbons (granular and cloths), a zeolite and a silica gel. This difference was attributed to the BET surface area and total porous volume which are larger for activated carbons than for the silica and zeolite adsorbents. A reduction in the L2 adsorption capacities of AC cloths up to ca. 40% was observed by the authors [20] when the regenerability issue was addressed by thermal treatment at 90 °C for three cycles, most probably due to the low temperature used. Indeed, Gilson et al. [21] achieved a 70% recovery applying a thermal regeneration at 200 °C while efficiency greater than 95% for L2 exhausted-activated charcoal were reported at 250 °C by Schweigkofler and Niessner [22]. The thermal regeneration of activated charcoal was found to be less effective for D5 with a loss up to 25% of the initial capacity, in similar conditions (250 °C for 20 min) [22]. Silica gel was reported in this study [22] to present similar adsorption capacities for L2 and D5 as activated charcoal with better thermal regeneration for both siloxanes.

It is generally accepted that the thermal regeneration of spent carbons is hampered by the conversion of siloxanes into by-products, e.g. silicon polymers and silica [23-27]. Finocchio and coworkers [24] have shown that D3 polymerizes at least partially on the carbon surface upon a laboratory adsorption experiment at room temperature giving rise to polydimethylsiloxane (PDMS). The growth of amorphous silica on AC was further observed together with PDMS when the adsorbent has been used to purify a real landfill biogas. The formation of siloxane polymers (mainly D5 with small amounts of D6 and D7) were also observed by Cabrera-Codony et al. [25] as a result of the D4 ring opening and further polymerization on spent AC adsorbents. The authors found that the textural properties of the studied ACs have little effect on the D4 polymerization contrary to what was observed for the adsorption properties. They related the polymerization of the adsorbed D4 to the oxygen content of the carbons acting as catalytic active centers for cyclosiloxane ring-opening polymerization and further propagation reactions [25-27].

In our previous study [28], upon the adsorption of D4 single component on different activated carbons presenting predominantly microporous structure (S_{μ}/S_{BET} higher than 0.70), the formation of polysiloxanolate/PDMS molecules is proposed to take place in the porous systems containing alkali metal cations which inhibits the regenerability. In the absence of such sites, the regeneration was complete. Based on these results, the objective of this work is to extend our investigation to other siloxanes in order to see if the extent of regeneration depends on the type of molecule: linear or cyclic structure, the number of $-\text{Si}(\text{CH}_3)_2-\text{O}-$ functional groups.

The dynamic adsorption of siloxanes as single component was studied at room temperature (20 ± 2 °C) by Gas Chromatography (GC) analysis. Five siloxanes namely L2, L3, L4, D4 and D5 were considered. Two commercial ACs were selected based on their opposite behavior with respect with D4 desorption upon thermal treatment [28]. The regenerability

issues were addressed by performing thermodesorption experiments on the spent ACs up to 400 °C. The evolution of the gas phase during thermal treatment was followed by Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).

To our knowledge, this is the first time such a comparative study is reported.

2. Experimental

2.1. Siloxane molecules and activated carbons

L2, L3, L4, D4 and D5 purchased from Sigma Aldrich were used for the adsorption experiments. Their main characteristics are given in [Table 2](#). The two commercial coal-based ACs studied were supplied by CHEMVIRON (Belgium), namely EnvironCarb AP4-50 and EnvironCarb STIX 4mm, here denominated as AP4 and STIX respectively. AP4 is a high temperature steam activated carbon used for the abatement of various organic compounds. STIX is an impregnated AC treated with alkaline solution and especially used for the removal of acid gases (H₂S, SO₂, HCl,...). These porous systems have been chosen on the basis of our previous study [28]: AP4 totally preserved its adsorption capacity for D4 during 3 adsorption-desorption cycles while STIX lost more than 50% of the initial adsorption capacity in similar conditions. The ACs samples were ground and sieved to obtain particle sizes in the range of 300 to 450 μm for dynamic adsorption tests and between 40 and 75 μm for DRIFTS experiments. Deep physicochemical characterization of ACs was previously reported [28]. Briefly, AP4 and STIX BET surface areas are equal to 991 and 766 m² g⁻¹ respectively. Both samples present narrow micropores (diameter lower than 1 nm) and pores in the range 1-3 nm. They are predominantly microporous with S_μ/S_{BET} varying between 0.7 (STIX) and 0.8 (AP4). XPS analysis revealed the presence of various surface oxygenated functional groups (similar in nature and amounts for both samples). Based on EDX, STIX presents more

inorganic impurities (11.1 wt%) than AP4 (3.4 wt%), the main impurity on STIX being K (6.6 wt%) while this impurity is at trace level on AP4 (0.02 wt %).

2.2. Measurement of adsorption capacity of AC through siloxane adsorption – thermodesorption cycles

Single component breakthrough adsorption experiments were carried out at room temperature (20 ± 2 °C). The gas mixtures were generated by injecting liquid siloxane into a N₂ flow (80 mL min⁻¹) to obtain 1000 ppm (v/v) of L2, L3 and D4, 200 ppm (v/v) of D5 and 50 ppm (v/v) of L4. These values were basically chosen taking into account the varying vapor pressures of the molecules at 25°C (Table 2) so that the time required to reach the adsorption equilibrium could be less than 1 day .

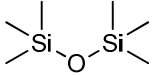
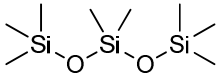
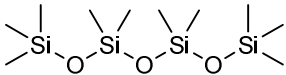
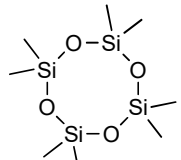
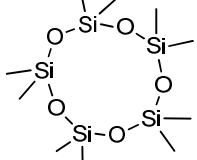
About 100 mg of AC samples were packed in a stainless steel tube (4.0 mm I.D x 47 mm long) sealed at both ends by quartz wool plugs. The bed height was 12 mm for STIX and 16 mm for AP4. Before adsorption, samples were heated at 150 °C under flowing N₂ (5 L h⁻¹) for 2 h. The concentration of siloxane at the outlet of the tube was monitored versus time using a Flame Ionization Detector (FID) from a Perkin Elmer GC “Autosystem”. The signal was converted into breakthrough curve using Total Chrom software.

The dynamic adsorption experiment was performed until complete saturation of sorbent bed as reported in our previous work [28]. The adsorption capacity at equilibrium defined as the quantity of adsorbed siloxane (in milligram) at saturation per gram of sorbent was calculated from the breakthrough curve according to the following equation:

$$\text{Equilibrium adsorption capacity} = \frac{Q}{m} (C_0 \cdot t_s - \int_0^{t_s} C(t) dt)$$

where Q is the inlet flow (mL min^{-1}), m the adsorbent mass (g), C_0 the siloxane initial concentration (mg mL^{-1}), $C(t)$ the siloxane outlet concentration at given time t and t_s the bed exhaustion time (min).

Table 2. Characteristics of siloxanes used in this study.

Substance	Formula (Abbreviation)	Structure	Molecular Weight ^[29,30] g mol ⁻¹	Vapor pressure at 25 °C (Pa) *	Melting point ^[30,31] (°C)**	Boiling point (°C)	Critical diameter nm***
Hexamethyldisiloxane	C ₆ H ₁₈ OSi ₂ (L2)		162.38	4120-5626 ^[22,30-33]	-59/-68	101/107 ^[19,22,31-33]	0.73 ^[26,27]
Octamethyltrisiloxane	C ₈ H ₂₄ O ₂ Si ₃ (L3)		236.53	445/520 ^[30-32,34]	-82/-86	153 ^[19,31,32]	
Decamethyltetrasiloxane	C ₁₀ H ₃₀ O ₃ Si ₄ (L4)		310.77	50/70 ^[30,31,34]	-68/-76	194 ^[19,31]	
Octamethylcyclotetrasiloxane	C ₈ H ₂₄ O ₄ Si ₄ (D4)		296.62	121-140 ^[22,30-34]	17.5	176 ^[19,22,31-33]	1.08 ^[26,27]
Decamethylcyclopentasiloxane	C ₁₀ H ₃₀ O ₅ Si ₅ (D5)		370.77	20-27 ^[22,30-34]	-38/-44	205/211 ^[19,22,31-33]	1.10 ^[26]

* several values found in this domain

** two different values found from the literature

*** The critical diameter is defined as the diameter of the smallest cylinder inside which the molecule fits [35]

Once the adsorption equilibrium was reached, the inlet gas was switched from the siloxane containing gas to N₂ flow for 16 h at room temperature until complete removal of siloxane from the gas phase. Afterwards, the regeneration of exhausted AC was performed by heating the sample up to 400 °C (5 °C min⁻¹) under N₂ flow. Three cycles of adsorption/thermodesorption were carried out for each adsorbent and each siloxane type. The adsorption capacity was measured for each cycle from breakthrough curves to evaluate the regenerability of AC (GC analysis). Additionally, a gravimetric method was used to measure the amount of sorbed compounds eventually retained after thermodesorption.

The column was disconnected from the line, plugged at both ends by stainless steel caps and weighed before the first adsorption step (after the pretreatment), after the 16 h purge in N₂ following the adsorption and after the thermodesorption step (after cooling). The amount of siloxane (in mg g⁻¹) retained during the adsorption step of each cycle was obtained by the difference of the weighed masses before adsorption and after adsorption+purge. The amount of retained compounds after thermodesorption step of each cycle was derived by the difference of the AC masses of the fresh (after pretreatment) and regenerated samples.

2.3. In situ FTIR study of gaseous compounds released during thermodesorption step

Gaseous compounds released during thermodesorption step (adsorbed siloxanes and products formed by their possible transformation) were investigated by in-situ DRIFTS. A Thermo Nicolet Nexus 6700 FTIR spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector was used. Experimental procedure details were previously reported [28,36]. Briefly, about 20 mg of a mixture of AC and KBr (mass ratio of 1:15) were introduced into Spectra Tech double cup environmental cell. The mixture was pretreated at 150 °C during 2 h under N₂ atmosphere before contacting for 1 h with the gas containing siloxane. The cell was then purged overnight under flowing N₂ (5 L h⁻¹) at room temperature in order to fully remove siloxane from the lines [36]. Afterwards, the thermodesorption

experiment was carried out by heating the exhausted sample up to 400 °C (flowing N₂, 5 °C min⁻¹). Spectra were collected every 4 min (interval of 20 °C) at a resolution of 4 cm⁻¹ using 64 scans and a scanning velocity of 1.889 cm s⁻¹. Only the spectral region between 1300 and 800 cm⁻¹ will be given below. Other regions were also analyzed but no further information could be derived.

3. Results and discussion

3.1. Measurement of siloxane adsorption capacity

The adsorption capacities of AC samples for L2, L3, L4, D4 and D5 measured from breakthrough experiments at 20 ± 2 °C and by gravimetric method are reported in [Table 3](#). Results concerning D4 adsorption, although already reported [28], are given here for the sake of clarity of the comparison with its linear counterpart (L4) and longer cyclic chain (D5).

Table 3. Adsorption capacities, determined by GC analysis and gravimetry (values between parentheses), of STIX and AP4 for different siloxanes (L2, L3, L4, D4 and D5) expressed in mg g⁻¹.

Siloxane	Adsorption capacity (mg g ⁻¹)	
	STIX	AP4
L2	103 (87)	161 (168)
L3	117 (111)	229 (219)
L4	162 (152)	290 (284)
D4	161 (155)	269 (273)
D5	146 (150)	245 (250)

Table 3 shows quite a good agreement between GC and gravimetric methods (2-6% variation between both measurements except when L2 is adsorbed on STIX). Irrespective of the AC sample, the mass of adsorbed siloxane increases with the increase of the chain length for the linear molecules while an opposite trend is found for cyclic ones. The values fall in the range already reported in the literature for L2 (10-350 mg g⁻¹), D4 (50-300 mg g⁻¹) and D5 (40-530 mg g⁻¹) [14–16,19,21]. To our knowledge, this is the first study reporting on L3 and L4 adsorption. It can be also derived that AP4 appears as a better adsorbent than STIX for all studied siloxanes.

3.2. Investigation of ACs regenerability through cycles of adsorption – thermodesorption

In order to address the ability of studied ACs to be regenerated, three adsorption/desorption cycles were carried out and the amount of adsorbed siloxane measured by both GC (breakthrough curve) and gravimetry. The siloxane adsorption measurements were performed at 20 °C until surface saturation while the desorption step was performed by thermal treatment of the exhausted AC samples under N₂ up to 400 °C. Tables 4 and 5 report the evolution of the adsorbed amounts of siloxane through different cycles as well as those being not desorbed during thermodesorption step. The values reported show an average difference of ± 8 mg g⁻¹ between GC and gravimetric analyses. In some scarce cases, the difference could reach ca. 20 mg g⁻¹, as for e.g. the adsorption of L2 on STIX. The loss of L2 (high volatility) during weighing could not be invoked to explain this variation between two methods since the opposite result was obtained with AP4. Average values were taken into account for the discussion since, even though differences exist between methods, the same conclusions could be drawn. From Table 4, it can be seen that the initial L2 adsorption capacity of STIX is preserved during three adsorption steps indicating 100% regeneration efficiency. The thermal desorption was less effective when considering the other studied siloxanes.

Table 4: Evolution of the adsorbed amounts of siloxane on STIX sample through different cycles. Experimental conditions: adsorption of siloxane (1000 ppm for L2, L3 and D4, 200 ppm for D5 and 50 ppm for L4) on 100 mg AC at room temperature (20 ± 2 °C) followed by the thermodesorption of the spent AC under N₂ up to 400 °C (5 °C min⁻¹).

Adsorbed molecule	Adsorbed amounts of siloxane (mg g ⁻¹)							
	GC analysis ¹			Gravimetric analysis ²				
	Ads.1	Ads.2	Ads.3	Ads.1	Residue 1	Ads.2	Residue 2	Ads.3
L2	103	106	98	84	0	85	0	89
L3	117	109	78	111	6	100	30	74
L4	162	127	99	152	23	121	40	99
D4	161	103	77	155	51	103	65	75
D5	146	101	84	150	18	124	40	99

¹ Values obtained from single component breakthrough adsorption experiments ² Amount of siloxane retained during the adsorption step of each cycle, which can be compared with that obtained by GC. The residue mass is obtained after each thermodesorption step by difference between the masses of fresh and regenerated ACs.

Table 5: Evolution of the adsorbed amounts of siloxane on AP4 sample through different cycles. Similar experimental conditions as described in [Table 4](#).

Adsorbed molecule	Adsorbed amounts of siloxane (mg g ⁻¹)							
	GC analysis			Gravimetric analysis				
	Ads.1	Ads.2	Ads.3	Ads.1	Residue 1	Ads.2	Residue 2	Ads.3
L2	161	165	164	168	0	166	0	167
L3	229	218	215	219	0	220	0	218
L4	290	252	236	284	18	246	20	240
D4	263	272	274	273	2	260	3	260
D5	245	236	211	250	12	239	20	236

Taking into account the average values between the GC and gravimetric measurements, after the third adsorption cycle, a loss of 33, 37, 38 and 52 % of the initial capacity was measured for L3, L4, D5 and D4, respectively.

AP4 (Table 5) shows better regenerability properties in comparison with STIX with complete recovery of the adsorption properties for L2, L3 and D4, and only 10 and 17 % loss of adsorption capacities for D5 and L4, respectively. The ability of the adsorbents to regenerate by thermal treatment seems not to follow the same trend for both ACs. However, it can be concluded that the less effective thermal regeneration is related with the presence of residues adsorbed in the porous systems as measured by gravimetry after each thermodesorption step.

These residues can be the result of an uncomplete desorption for the siloxanes with low volatility such as L4 and D5 (Table 2). The formation of polymeric species such as polysiloxanolate, polydimethylsiloxane (PDMS) or α - ω -silanediols by transformation of adsorbed D4 in the adsorbents porosity during adsorption and/or thermodesorption steps was also proposed [25-28] and could account for the formation of these residues.

3.3. In situ DRIFTS study of siloxane thermodesorption from AC

In-situ DRIFTS was used to study the gaseous compounds released during thermodesorption steps (adsorbed siloxanes and products formed by their possible transformation). Spectra of pure siloxane molecules (L2, L3, L4, D3, D4, D5) in gas phase between 1400 and 700 cm^{-1} are given in Fig. 1. The positions and assignments of the vibration bands in this region are reported in Table 6. The positions are similar with those reported in the literature [28 and references therein]. The bands which allow to distinguish between different types of siloxanes in the gas phase are the Si-O-Si stretching and CH_3 rocking modes.

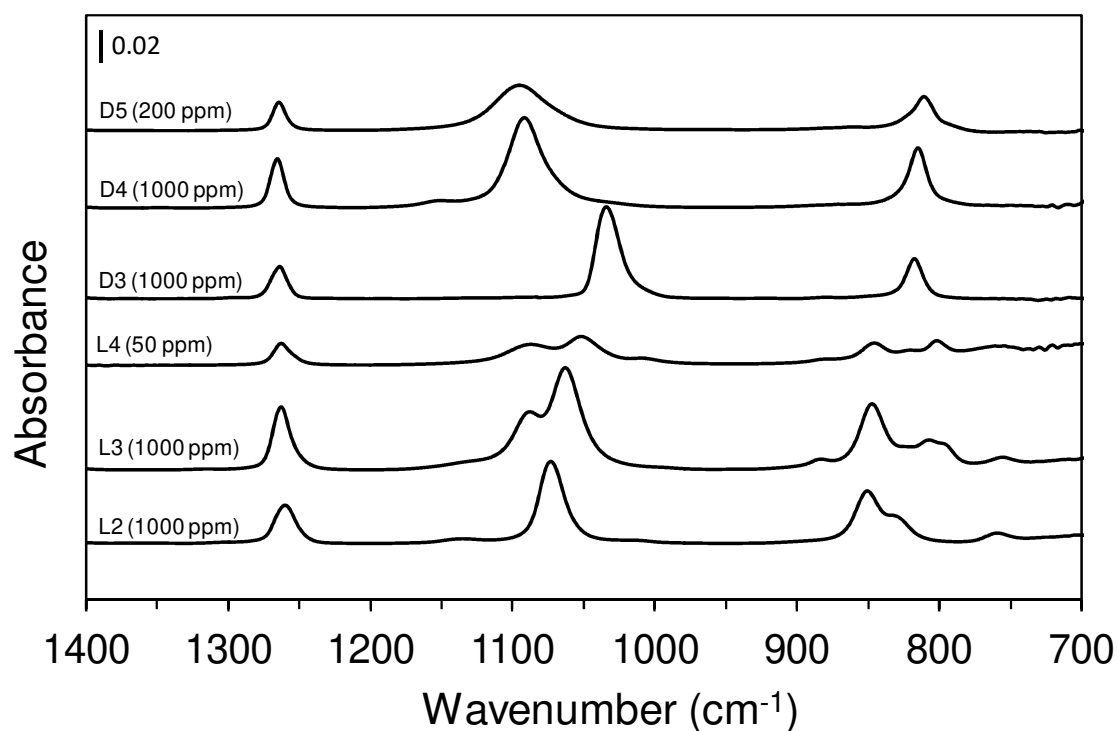


Fig. 1. IR spectra of L2, L3, L4, D3, D4 and D5 gas in the 1400-700 cm^{-1} region at 20 ± 2 °C. Siloxane concentration in N_2 flow (5 L h^{-1}): 1000 ppm (v/v) for L2, L3, D3 and D4, 200 ppm (v/v) for D5 and 50 ppm (v/v) for L4.

Table 6. Assignment of IR stretching, bending and rocking vibrations of different linear and cyclic siloxanes.

Molecule	Si-CH ₃ bending	Si-O-Si stretching	CH ₃ rocking
L2	1261	1072	850
L3	1263	1088, 1063	847, 807
L4	1263	1088, 1052	845, 802
D3	1264	1035	818
D4	1265	1092	815
D5	1264	1095	811

It can be remarked that for D4 and D5 these two bands are separated by less than 4 cm^{-1} , which is too small to differentiate between these two molecules in the case they are both present in the gas phase.

3.3.1. Cyclic molecules

The spectral evolutions during D4 and D5 thermodesorption over AP4 and STIX are shown in [Figs. 2](#) and [3](#) respectively. After adsorption of D4 (resp. D5) over AP4 and subsequent purge in N_2 at $20\text{ }^\circ\text{C}$, the spectra reveal three bands of very weak intensity at 1262 cm^{-1} (for D4 and D5), 1089 cm^{-1} (1093 cm^{-1} for D5) and 816 cm^{-1} (812 cm^{-1} for D5) attributed respectively to the bending mode of Si- CH_3 bonding, the asymmetric stretching mode of Si-O-Si bonding, the bending and rocking mode of CH_3 bonding of adsorbed D4 and D5. For STIX sample, these bands appear at 1262 , 1087 and 816 cm^{-1} for adsorbed D4 and 1262 , 1088 and 812 cm^{-1} for D5. All these bands are slightly shifted with respect to the gas phase, which could be due to the interaction with the adsorbent.

During the thermal desorption over AP4 ([Fig. 2](#)), the intensity of characteristic bands of D4 and D5 in gas phase increases continuously up to 200 and $300\text{ }^\circ\text{C}$ respectively before a progressive decrease up to $400\text{ }^\circ\text{C}$. At $400\text{ }^\circ\text{C}$, bands of D4 totally disappear while bands of D5 are still observable. No other siloxane species among those given in [Table 6](#) could be detected. It can be concluded that heating saturated AP4 sample under N_2 would release exclusively D4 or D5 without any transformation. The presence of D5 in gas phase at $400\text{ }^\circ\text{C}$ indicates its incomplete desorption, which agrees with the residual mass measured by gravimetric method ([Table 5](#)).

During the thermal desorption of D4 (resp. D5) over STIX ([Fig. 3](#)), the same trend as for AP4 is observed up to $120\text{ }^\circ\text{C}$, which suggests the only release of D4 (resp. D5) in the gas phase without transformation.

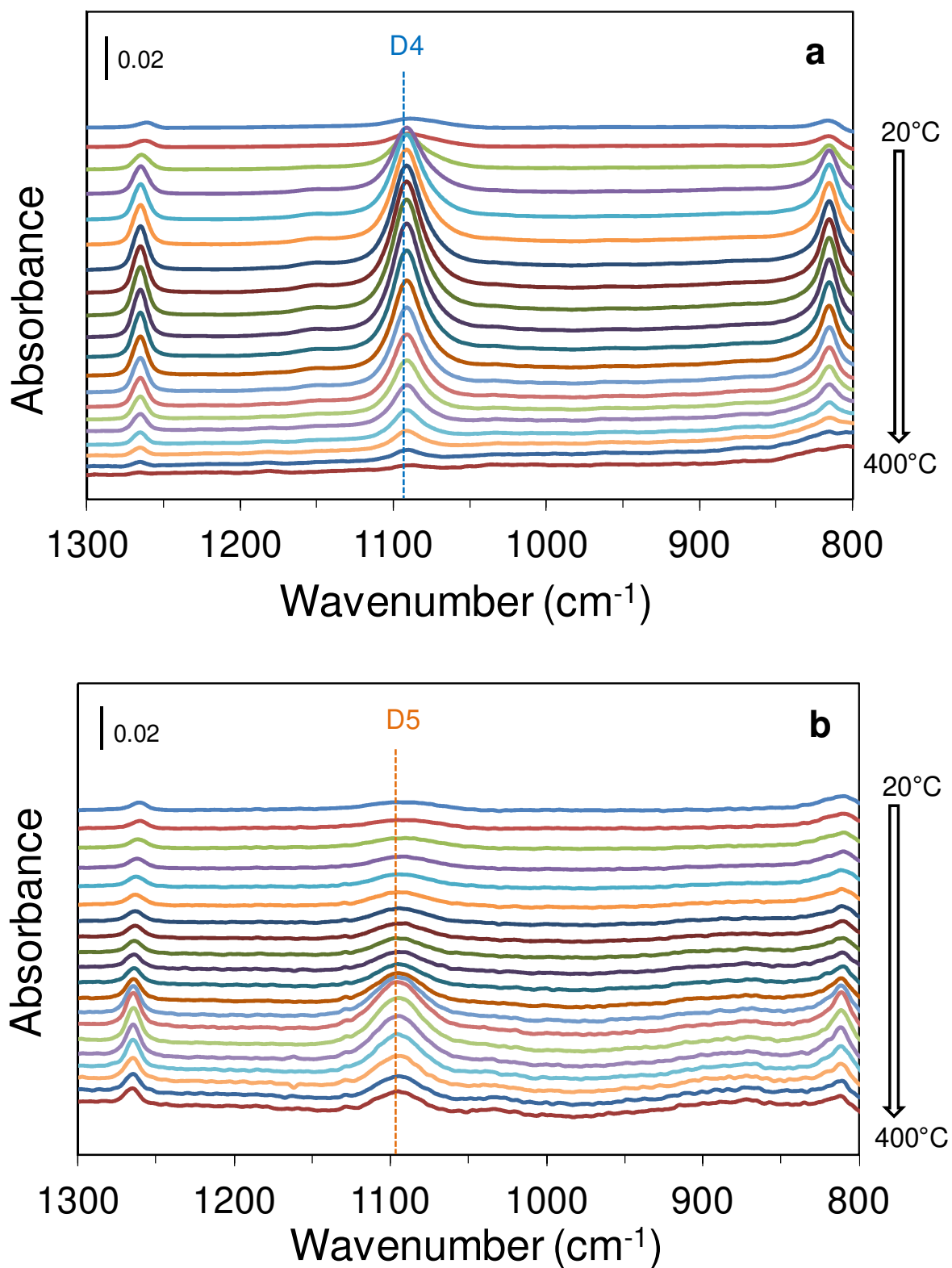


Fig. 2. IR spectra of thermodesorption of D4 (a) and D5 (b) on AP4 during the thermodesorption in the range of 20 – 400 °C (heating rate: 5 °C min⁻¹) under N₂ flow (5 L h⁻¹). Spectra collected every 20 °C are shown.

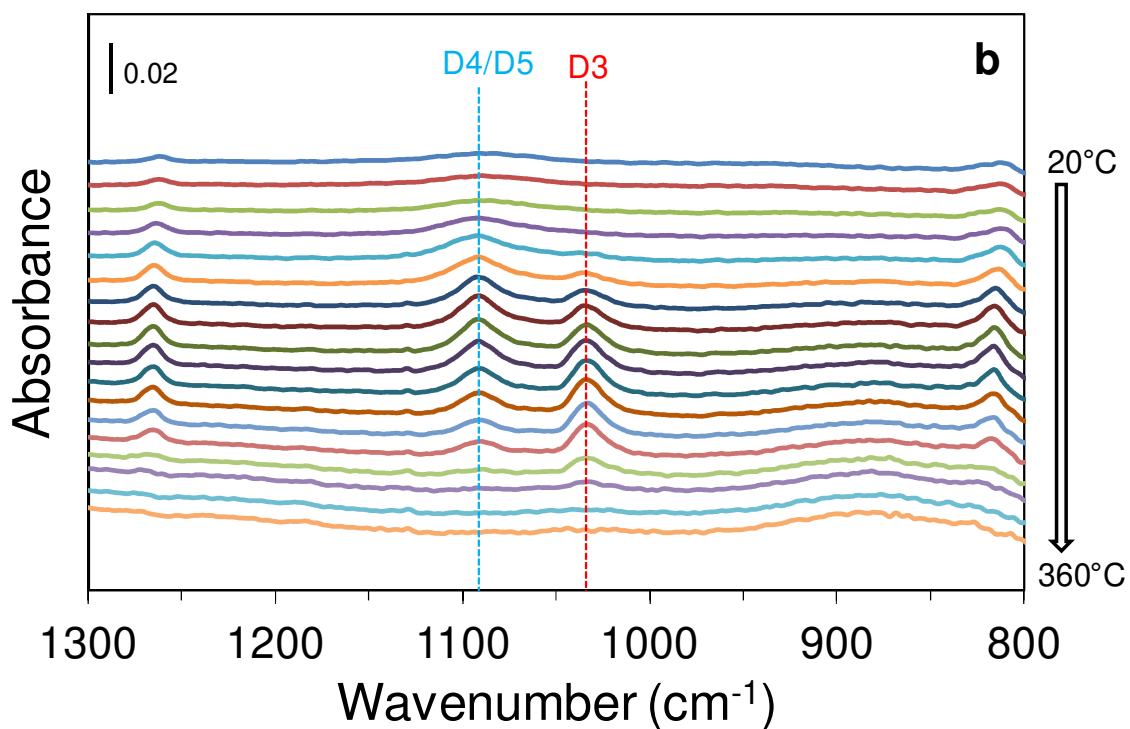
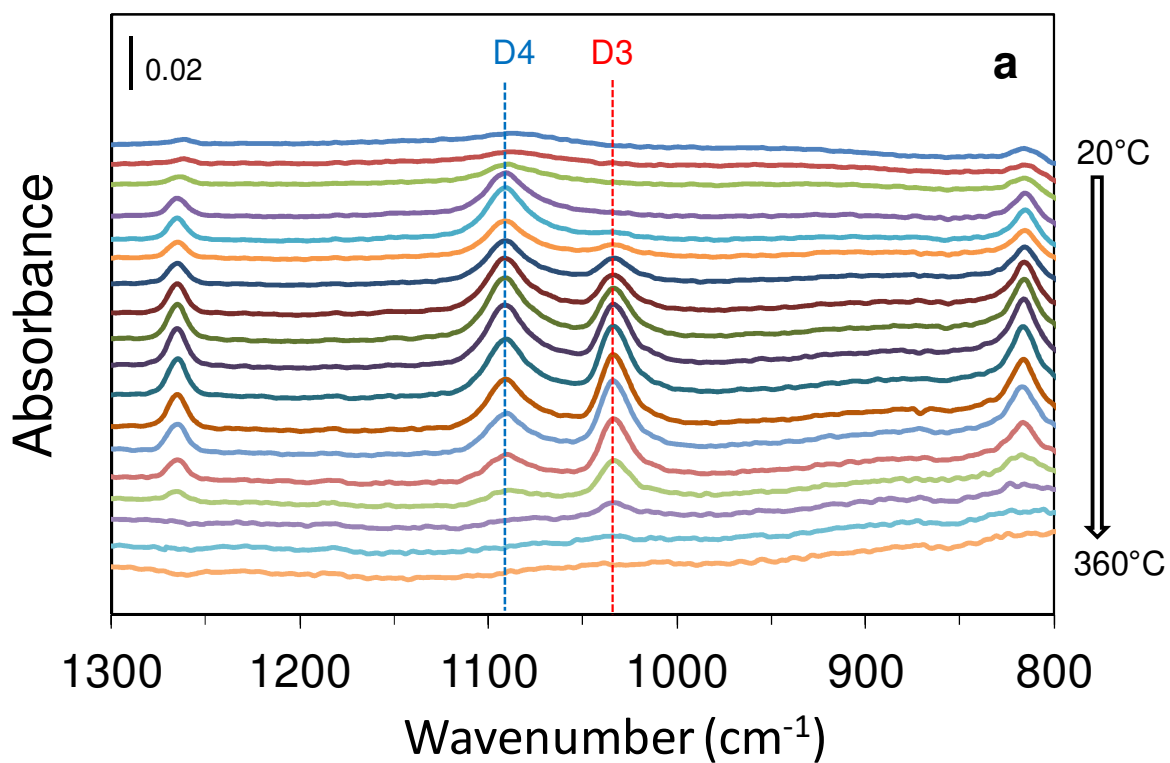


Fig. 3. IR spectra of thermodesorption of D4 (a) and D5 (b) on STIX during the thermodesorption in the range of 20 – 400 °C (heating rate: 5 °C min⁻¹) under N₂ flow (5 L h⁻¹). Spectra collected every 20 °C are shown.

Above 120 °C for both molecules, a new band at 1035 cm⁻¹ progressively develops up to 240 °C before decreasing in intensity, being fully depleted at 320 °C. This band can be assigned to the asymmetric stretching mode of Si-O-Si bonding of D3 gas. The appearance of D3 gas during D4 thermodesorption over STIX was previously related to the decomposition of polysiloxanolate/polydimethylsiloxane (PDMS) [28,37,38]. It can be concluded that similar transformations would undergo with D5 adsorbed on STIX during thermal treatment.

The intensity of the bands at 1092/1095 cm⁻¹ (characteristic of D4/D5 gases) and at 1035 cm⁻¹ (characteristic of D3 gas) was normalized to their respective maximum intensity during thermal treatment after the adsorption step over STIX at 20 °C. The evolution of the normalized intensity of these bands is reported in Fig. 4. Results of D4 desorption were already reported and discussed [28]. They are given here for comparison with D5. Briefly D4 desorbs between 40 and 120 °C without any significant transformation (negligible D3 release) while above this temperature, the products released (D3, D4) would result from the decomposition of polysiloxanolate/PDMS.

For D5 desorption, contrary to D4, the evolution of the 1095 cm⁻¹ band intensity only shows a broad peak between 60 and 300 °C with a maximum at around 180 °C. The onset temperature of D5 desorption is higher (20 °C difference) than for D4 desorption. The lower volatility of D5 compared to D4 would explain the shift and the broadening of the desorption peak of unreacted D5 towards higher temperatures. The appearance of D3 gas starts from 80 °C, being observed until ca. 350 °C. The release of D3 is indicative of the conversion of adsorbed D5 into polymerized species and their further decomposition. This phenomenon would occur simultaneously to the desorption of decomposition products, i.e. D3, D5 and possibly D4. The maximum rate of D3 desorption occurs at ca. 240 °C, that is the same temperature as for D4 thermodesorption. Above ca. 350 °C, no more release in gas phase could be observed, similarly to the experiment with D4.

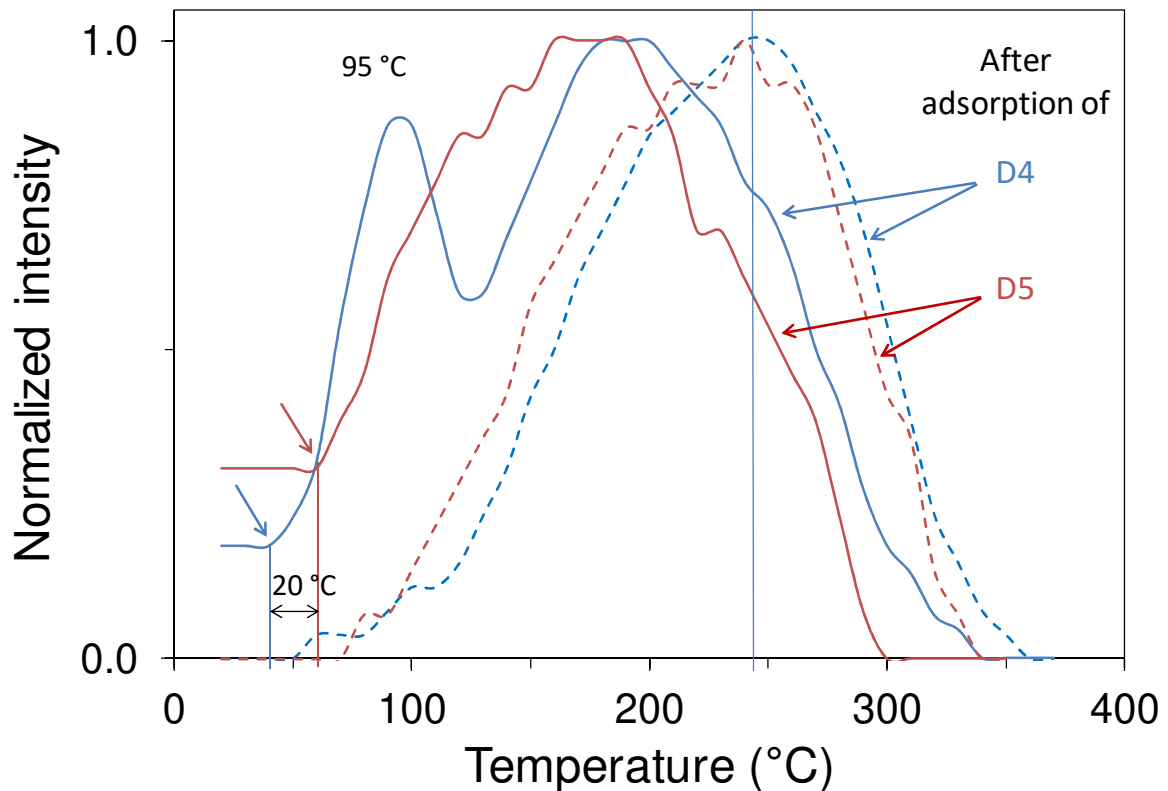


Fig. 4. Normalized variation of the intensity of the bands of D4 and D5 (1092 and 1095 cm^{-1}) and D3 (1035 cm^{-1}) during thermodesorption experiments after D4 and D5 adsorption over STIX. The desorption compounds from D4-exhausted AC are given in blue while those from D5-exhausted AC are in red. D4 and D5 desorption profiles are plotted as solid lines while D3 desorption profiles appear as dashed lines.

These results confirm the importance of the choice of the AC adsorbent for cyclic siloxanes removal from biogas in view of its regeneration by thermal treatments. The behavior of D5 appears very similar to that of D4 in terms of reactivity. However, in the absence of reactivity with the AC surface, D5 requires higher desorption temperatures than D4 in order to reach the complete regeneration of the adsorbent, which may be primarily attributed to its lower volatility.

3.3.2. L2, L3 and L4 thermodesorption

Fig. 5 and Fig. 6 exhibit the spectral evolution during L2, L3 and L4 thermodesorption from AP4 and STIX, respectively. As already observed for cyclic molecules, spectra of AP4 and STIX samples show, after outgassing overnight in N₂ at 20 °C following the adsorption step, bands of weak intensity corresponding to adsorbed L2, L3 and L4. These bands are slightly shifted with respect to that of the gas phase molecules due to the interaction with the AC surface. For AP4 (Fig. 5), desorption of linear siloxanes leads to the appearance of bands respectively at 1263, 1072 and 850 cm⁻¹ for L2, 1263, doublets at 1088 – 1063 and 847 – 807 cm⁻¹ for L3, 1263, doublets at 1086 – 1052 and 845–802 cm⁻¹ for L4. These bands correspond respectively to the stretching vibration of Si-CH₃ bonding, stretching vibration of Si-O-Si bonding and rocking vibration of CH₃ bonding of these molecules in gas phase. With increasing temperature, the intensity increases progressively up to a maximum before decreasing. Similar onset temperatures of desorption are observed irrespective of the siloxane (40 °C) while the maximum depends on the adsorbed molecule: ca. 120, 160 and 200 °C for L2, L3 and L4 respectively. Complete depletion of these bands can be observed at ca 300 °C for L2 and 360 °C for L3, which suggests the complete desorption of L2 and L3, in agreement with complete regeneration of AP4 observed during sorption cycles (Table 5). The presence of L4 in gas phase is consistent with the residual mass measured by gravimetric method. This can be explained by the low volatility of L4. The key point is that linear siloxanes adsorbed on AP4 can be desorbed without any transformation, thus allowing complete regeneration of the adsorbent by thermal treatment.

Fig. 6a shows the evolution of IR spectra for L2 thermodesorption between 20 and 360 °C on STIX in the region 1300-800 cm⁻¹. The development of bands at ~1260, ~1070 and ~850 cm⁻¹ for T ≥ 60 °C indicates the only release of L2 gas from the sample.

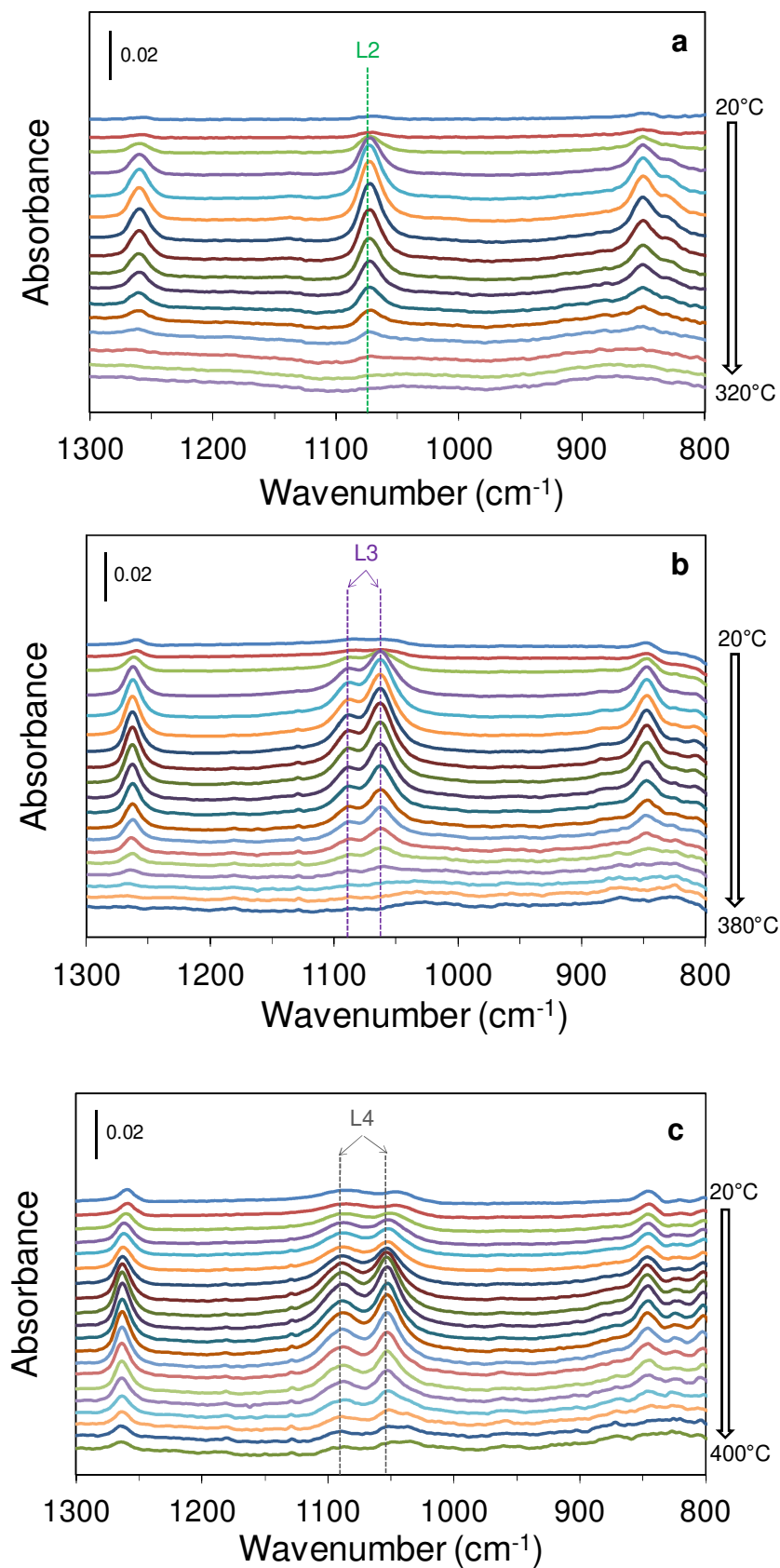


Fig. 5. IR spectra of thermodesorption of L2 (a), L3 (b) and L4 (c) on AP4 during the thermodesorption in the range of 20 – 400 °C (heating rate: 5 °C min⁻¹) under N₂ flow (5 L h⁻¹). Spectra collected every 20 °C are shown.

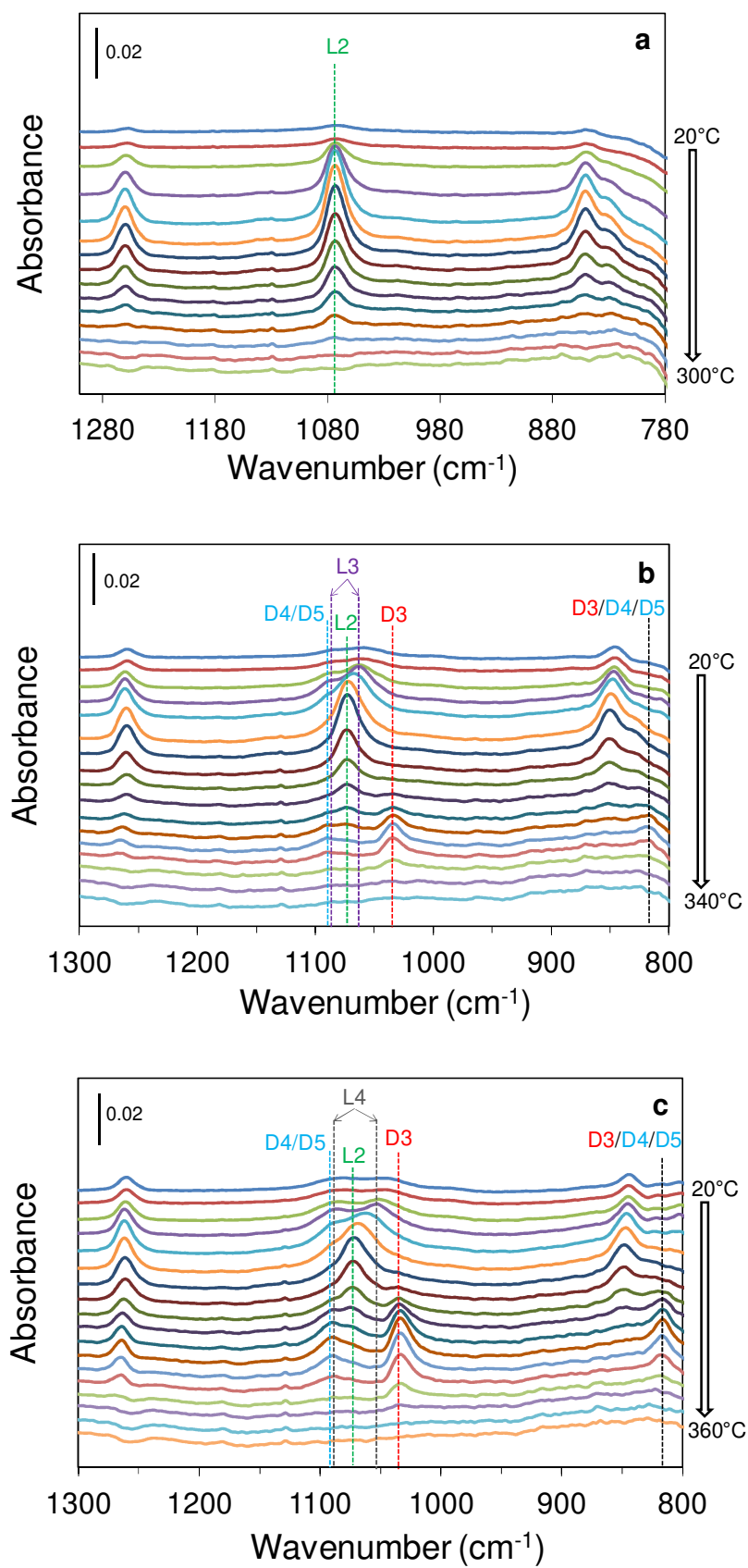


Fig. 6. IR spectra of thermodesorption of L2(a), L3(b) and L4(c) on STIX during the thermodesorption in the range of 20 – 400 °C (heating rate: 5 °C min⁻¹) under N₂ flow (5 L h⁻¹). Spectra collected every 20 °C are shown.

The maximum concentration is obtained at 100 °C. The release of L2 is no more observed above 280 °C. Comparing these results with those reported in [Table 4](#), it can be concluded that STIX is completely regenerated, L2 fully desorbing without transformation. Contrary to L2, thermodesorption of L3 ([Fig. 6b](#)) and L4 ([Fig. 6c](#)) is accompanied by desorption of other siloxanes than the adsorbed ones, suggesting some transformation during adsorption and/or thermodesorption processes. For L3 experiment, the appearance of bands at ~1260, ~1090, ~1060 and ~850 cm⁻¹ between 60 and 100 °C indicates the release of L3 gas. Above 100 °C and up to 180 °C no more L3 evolves from the sample, being replaced by L2 gas (bands at ~1260, ~1070 and ~850 cm⁻¹). L2 desorption proceeds up to 260-280 °C. From 200 °C and up to 300 °C, the development of bands at ~1260, ~1035 and ~820 cm⁻¹ attributed to D3 gas is observed together with a band of very weak intensity at 1087 cm⁻¹ attributed to other cyclic siloxanes (D4, D5, ...).

For L4 experiment, the same sequence occurs with the release of the adsorbed molecule (L4) followed by the appearance of L2, D3 and larger cyclic siloxanes in gas phase. L4 desorbs in the range 40-120 °C, L2 is observed between 100 and 280 °C, D3 appears between 140 and 340 °C and larger cyclic molecules between 180 and 300 °C.

It can be concluded that, on STIX, desorption of linear siloxanes except L2 is accompanied by the release of mainly L2 and D3 together with larger cyclic molecules, which suggests some transformation of adsorbed molecules.

The absence of any release in gas phase above 340 °C together with the decrease of the adsorption capacity ([Table 4](#)) can be explained by the formation of low volatile species in the porosity of STIX. The literature provides many reviews on the synthesis of linear polysiloxanes by ring opening polymerization of cyclic organosiloxanes and polycondensation of difunctional organosilanes or oligosiloxanes [39]. The conversion of linear siloxanes into high molecular weight polymers by interaction of siloxane with

silanolate, which allows the siloxane bond cleavage, was also reported [40]. The transformation of L3 and L4 observed over STIX during thermodesorption in the present study is to our knowledge the first observation of the reactivity of these molecules on activated carbons. It is proposed that the catalytic sites responsible for their transformation are the same as those involved in the ring opening polymerization of D4 and D5, tentatively attributed to strong basic centers associated with K. Both linear and cyclic molecules are produced. The observed release of L2 as primary product being formed during thermal desorption of adsorbed L3 and L4 may account for the cleavage of a Si-O bond in the siloxane chain. L2 was previously reported as a product of decomposition of L4 and L5 [20].

It must be remarked that the conversion of L3 and L4 seems to depend on the presence of specific sites at the AC surface since no such phenomenon occurs upon thermodesorption of AP4 sample. The release of cyclic molecules (D4, D5, ...) at higher temperatures would indicate that, besides the breaking of L3 and L4 into L2, polymerization reactions would proceed as well, being possibly favored by increased temperatures of the thermal treatment. High molecular weight linear polymers are proposed to be formed as revealed by the release of D3, the main decomposition product of such molecules, and D4/D5.

Fig. 7 shows the influence of the siloxane type on the AP4 and STIX regenerability after three siloxane adsorption/thermodesorption cycles. AP4 exhibits complete recovery efficiency for L2, L3 and D4 and more than 80% for L4 and D5. This exceptional behavior can be explained by the non transformation of these molecules during the adsorption/desorption cycles. The lower performance with L4 and D5 would be due to the low volatility of these molecules (Table 2). Higher temperatures or longer treatment durations could be appropriate to complete regeneration. On the contrary, STIX shows regeneration efficiency varying from 100% for L2 down to ca. 55% for D4, L4 and D5. This can be related to the reactivity of the molecules on the surface of STIX. To this respect L2 appears as a stable molecule. From Fig. 7, it could be

proposed that the reactivity would basically depend on the chain length, irrespective of the geometry (linear or cyclic). Based on characterization of this material reported elsewhere [28] the sites responsible for siloxanes conversion could be attributed to the presence of strong basic centers associated with surface alkali impurities. This could impact both regenerability issues, and adsorption capacity if conversion takes place at room temperature during adsorption as shown in [25]. Even though L3 and L4 are present in biogas in lower amounts than D4, this is of importance in the overall adsorption/desorption process since impacting the access of D4/D5 to the porosity.

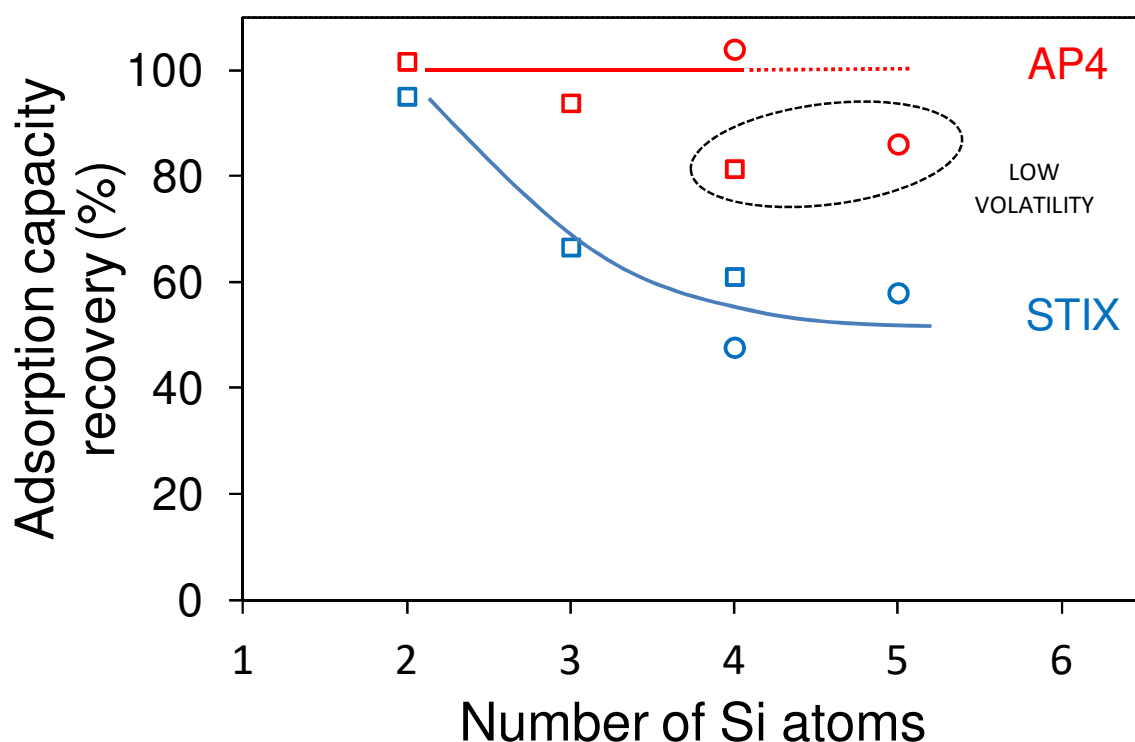


Fig. 7. Influence of the siloxane chain length and linear/cyclic type on the AP4 and STIX regenerability after three siloxane adsorption/thermodesorption cycles (expressed in % of the initial adsorption capacity). Squares: linear siloxanes; circles: cyclic siloxanes.

4. Conclusion

In this paper, the adsorption and thermal desorption properties of two commercial ACs, namely STIX and AP4, were studied using linear (L2, L3, L4) and cyclic (D4, D5) siloxanes. AP4 presents adsorptive and regenerability properties that make this material compatible for biogas purification from siloxanes contrary to STIX. This is due to the absence of surface sites responsible for ring opening of cyclic molecules and Si-O bond cleavage of linear ones giving rise to further polymerization and formation of low volatile compounds. For the AC containing such sites, only L2 is stable enough not to undergo further transformation. L3 and L4 are converted into L2 as primary product above 100 °C. Desorption of D3, D4 and D5 accounts for their further transformation into longer chain molecules blocking the porosity. The presence of strong basic sites associated with surface alkali impurities is thought to be responsible for the reactivity of siloxanes. The reactivity increases with the chain length irrespective of the geometry (linear or cyclic). This is the first study showing the reactivity of linear siloxanes and their importance on the biogas purification.

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Adsorption of linear and cyclic siloxanes on activated carbons for biogas purification: sorbents regenerability

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