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## Exploring the potential of infrared spectroscopy on the study of the adsorption/desorption of siloxanes for biogas purification

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### ABSTRACT

A commercial activated carbon (AC) was characterized by physicochemical methods. The AC adsorption/desorption properties and the adsorbent regenerability were evaluated for the removal of octamethylcyclotetrasiloxane (D4), a common siloxane impurity in biogases. *In situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was employed to investigate the adsorption of D4 on AC at room temperature and its thermodesorption up to 300 °C. The AC was activated in N<sub>2</sub> at varying temperatures within the 25–300 °C interval. The striking feature is the polymerization of D4 observed during the desorption experiment followed by the release of PolyDimethylSiloxane (PDMS) in the gas phase. The thermal treatment before adsorption is proposed to influence the D4–AC interaction.

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### 1. Introduction

Biogas is considered as a new clean fuel for the replacement of fossil fuels in many applications such as production of heat or steam, electricity generation or vehicle fuel [1,2]. Generally, it is produced in landfills or waste water treatment plant by anaerobic digestion of organic material in presence of anaerobic bacteria [1,3]. It contains mainly methane (from 40 to 60%) and carbon dioxide (from 40 to 55%) with small amounts of nitrogen-based compounds, oxygen and water. Depending on the feedstock, biogas can also contain trace amounts of hydrogen sulfide, halogenated and organic silicon compounds (e.g. siloxanes) which can cause maintenance issues with downstream equipment [4,5]. For the versatile use of biogas as fuel, it is necessary to remove harmful impurities that affect its utilization as an energy source. For example, siloxanes, volatile methylated organosilicon compounds (VMS) containing Si–O bonds [6], convert into silicon dioxide during combustion which causes a build-up of matter on the engine surfaces, and subsequently the decrease of the system efficiency [7].

The sources of siloxanes are various, such as hygiene, health care and industrial products [7]. Researches on the content of organic silicon compounds in biogas showed the presence of both linear- (hexamethyldisiloxane (L2), octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5)) and cyclic- (hexamethylcyclotrisiloxane (D3), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6)) siloxanes [8]. Among them, D4 and D5 are found to be the most abundant compounds in biogas [6]. Landfill gas usually contains more D4 than D5 since D4 has higher volatility [8].

With increasing biogas utilization as a replacement of fossil fuel, the removal of siloxanes at industrial scale is becoming a major challenge in both technical and economic aspects. Several techniques for siloxanes removal have been tried and some of them have been commercialized [9]. Among these techniques, the adsorption on activated carbon (AC) has proved to be the most efficient and cost effective method to remove siloxanes [10,11]. Several studies have been carried out to assess the AC properties for an optimal performance. Textural properties are shown to influence the adsorption capacity. The adsorption capacity is improved by an increased BET surface area [10,12] and an average pore size in the range 1.7–3.0 nm [10]. Nevertheless, few studies are dedicated

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to understanding the adsorption mechanism. Finocchio et al. [13] reported that D3 polymerized into PolyDimethylSiloxane (PDMS) after the adsorption on AC at room temperature in a laboratory test. At pilot scale, an exhausted AC after contact with real biogas showed the formation of amorphous silica [13]. Cabrera-Codony et al. [14] studied the adsorption of D4 and observed the formation of larger cyclosiloxanes like D5, D6 and D7 by GC–MS analysis of organic compounds extracted by hexane from spent AC. However, the adsorption mechanism still remains unknown. The authors proposed the transformation of D4 into larger cycles involving the ring opening but the existence of intermediate species was not confirmed in their study.

From an economic and environmental point of view, the regeneration of spent sorbent is needed. The most common way to regenerate spent sorbent is the thermal treatment (100–250 °C) to release all volatile compounds [15–17]. However, the regeneration efficiency has been reported with varying degrees of success. Ortega and Subrenat [15] have studied the adsorption of L2 on AC at 25 °C and desorption by heating at 100 °C. During the first 3 adsorption-desorption cycles, the adsorption capacity was observed to progressively decrease. Afterwards the adsorption capacity remained constant, being equal to 75% of the initial adsorption capacity. Gislou et al. [16] studied the adsorption of L2 at 30 °C followed by desorption up to 200 °C over 5 kinds of ACs. Repeating adsorption-desorption cycles was found to degrade the adsorption capacity down to about 70% of the initial capacity. Although there is some agreement in the literature on the degradation of adsorptive properties after thermal regeneration, little information could be found about the factors affecting this process.

In this perspective, the Fourier transform infrared (FTIR) spectroscopy seems to be useful to investigate the mechanism of the adsorption/desorption processes. The present paper aims at studying D4 adsorption at room temperature on a commercial activated carbon, and its desorption at various temperatures by *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The objective is to gain insight into the possible transformations of D4 throughout the adsorption/desorption process and identify possible parameters affecting the regenerability of the adsorbent. The influence of the thermal pretreatment before adsorption is also addressed. The AC used in this study was characterized in terms of the elemental composition, thermogravimetric characteristics, surface area, pore size distribution, and oxygen-containing functional groups composition. D4 was selected in this work as a target siloxane compound due to both its high content, which hinders the use of biogas in some energy recovery equipments, and issues concerning its impact on human health and on the environment. The use of *in situ* DRIFTS as a tool for studying adsorption/desorption processes on AC is finally evaluated.

## 2. Experimental

### 2.1. Materials

Octamethylcyclotetrasiloxane (D4) purchased from Sigma Aldrich was used for the adsorption experiments. The activated carbon sample was STIX (coal based AC) being supplied by CHEMV-IRON (Belgium). The AC was ground and sieved to 40–75  $\mu$ m.

### 2.2. Physicochemical characterizations

The pores texture of STIX was investigated from N<sub>2</sub> adsorption/desorption isotherm at –196 °C by ASAP 2020 Micromeritics apparatus. Prior to the measurement, sample was outgassed by heating at 300 °C under vacuum during 5 h. Specific surface area ( $S_{\text{BET}}$ ) was calculated from the BET (Brunauer – Emmet – Teller) standard

equation. The micropore volume ( $V_{\mu}$ ) and the micropore surface area ( $S_{\mu}$ ) were obtained via t-plots. Mesopore surface area was calculated by subtracting the micropore area from the total surface area. The average pore diameter ( $D_p$ ) and the pore size distribution were calculated using Density Functional Theory method.

X Ray Diffraction (XRD) analysis was performed on a Bruker D8 Advance A25 with CuK $\alpha$  ( $\lambda = 0.1541$  nm) radiation and Lynx-Eye detector. The X-ray pattern was recorded for  $2\theta$  from 4 to 80° at a scan rate of 0.04°/s and the obtained spectra were analyzed using EVA – DIFFRAC software.

The sample microstructure was examined by scanning electron microscopy (SEM). The SEM micrographs were obtained from a JEOL JSM 5800LV microscope. The sample was poured as thin layers on double-sided adhesive carbon discs on the sample holder, and metalized with gold to avoid charging. Also, an Energy-dispersive X-ray (EDX) analysis was carried out to evaluate the impurities of the carbon powder. The EDX results were further confirmed by chemical analysis. For this, the residual ashes obtained after AC oxidation were mixed with Li tetraborate in Pt-Au crucibles, heated at 1100 °C before dissolution in HCl solution (20%). The solution was then analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Activa instrument from Horiba Jobin Yvon).

Further, elemental analysis was used to determine the carbon, hydrogen, nitrogen and sulfur composition of the sample. The experiment was carried out in a Thermo Fisher Flash 2000 CHNS analyzer.

The thermal stability measurements and the ash content determination were performed by heating the powder from room temperature to 1000 °C (10 °C/min) under an atmosphere containing 20% O<sub>2</sub> in N<sub>2</sub> (40 mL/min). The experiment was conducted with a Pyris Diamond TG/DTA analyzer from PerkinElmer and both TG and heat flow curves could be recorded simultaneously as the temperature increased. The plateau in the mass loss variation observed at the end of the experiment indicated that the heat treatment applied ensured that the material fraction contained in the sample was completely oxidized and transformed into gaseous products and residual ashes.

To study the thermal stability of the AC in inert atmosphere, another TG experiment was carried out using a nitrogen flow (40 mL/min, room temperature – 900 °C, 10 °C/min).

Surface functional groups were investigated by FTIR and X-Ray photoelectron spectroscopy (XPS) analysis. The infrared spectra were obtained in transmission mode using a FTIR spectrometer Nicolet 6700. Prior to analysis, a 16 mm sample pellet was prepared by grinding 1 mg of AC together with 150 mg of KBr. The blend is pressed under 3 tons/cm<sup>2</sup>. The spectra were obtained at a resolution of 4 cm<sup>–1</sup>. The XPS analysis was performed with a KRATOS Axis Ultra DLD spectrometer utilizing a monochromatized Mg K $\alpha$  X-ray source (1486.6 eV). The survey scan spectra were collected with an energy pass of 160 eV, whereas the high-energy resolution spectra were performed with the pass energy of 20 eV.

### 2.3. Adsorption/desorption experiments

The adsorption/desorption experiments were carried out by using a homemade apparatus. For the adsorption, a mixture of about 1000 ppmv D4 in N<sub>2</sub> (total flow of 5 L/h) was produced by injecting D4 liquid in a syringe pump (1  $\mu$ L/min) into the nitrogen flow. The concentration of the siloxane (12 g/m<sup>3</sup>) was much higher than in the biogas (up to 4.3 mg/m<sup>3</sup> for D4) [18] for shortening the adsorption process. The D4-containing flow was introduced into a DRIFTS cell containing about 20 mg mixture of STIX and KBr (ratio 1:15). Adsorption experiments were performed at room temperature using a double cup environmental chamber of Spectra Tech installed on a Thermo Nicolet Nexus 6700 FTIR spectrometer. One compartment contained the sample mixture and the other only KBr

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