Siloxanes removal from biogas by high surface area adsorbents

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ABSTRACT

Biogas utilized for energy production needs to be free from organic silicon compounds, as their burning has damaging effects on turbines and engines; organic silicon compounds in the form of siloxanes can be found in biogas produced from urban wastes, due to their massive industrial use in synthetic product, such as cosmetics, detergents and paints.

Siloxanes removal from biogas can be carried out by various methods (Mona, 2009; Ajhar et al., 2010 May; Schweigkofler and Niessner, 2001); aim of the present work is to find a single practical and economic way to drastically and simultaneously reduce both the hydrogen sulphide and the siloxanes concentration to less than 1 ppm. Some commercial activated carbons previously selected (Monteleone et al., 2011) as being effective in hydrogen sulfide up taking have been tested in an adsorption measurement apparatus, by flowing the most volatile siloxane (hexamethyldisiloxane or L2) in a nitrogen stream, typically 100–200 ppm L2 over N_2, through an activated carbon powder bed; the adsorption process was analyzed by varying some experimental parameters (concentration, grain size, bed height). The best activated carbon shows an adsorption capacity of 0.1 g L2 per gram of carbon. The next thermogravimetric analysis (TGA) confirms the capacity data obtained experimentally by the breakthrough curve tests.

The capacity results depend on L2 concentration. A regenerative carbon process is then carried out by heating the carbon bed up to 200 °C and flushing out the adsorbed L2 samples in a nitrogen stream in a three step heating procedure up to 200 °C. The adsorption capacity is observed to degrade after cycling the samples through several adsorption–desorption cycles.

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1. Introduction

Siloxanes have been classified as unwanted and harmful pollutants in biogas originated from gasification of anthropic wastes (Mona, 2009; Ajhar et al., 2010). The reason lies in the mechanical corrosion caused by organic silicon compounds produced from the oxidation of siloxanes during combustion.

Siloxanes are a class of chemical compounds, linear or closed chains of functional groups $(R_2SiO)_n$, where R is either a hydrogen or alkyl group. The total volatile siloxanes content, and their relative volumetric percentage in biogas vary largely, depending on biogas origin: generally speaking, as they are diffusely used in a large variety of cosmetic and detergent products, their content is extremely low in biogas from agricultural wastes, whilst anthropic biogas can contain a siloxane content as large as 3–25 mg/m^3 (0.6–5 ppm) Mona, 2009. Cyclic siloxanes octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) are the most common compounds in waste treatment plants, D4 and L2 in landfills (Rosi et al., 2010).

It has been recognized that the presence of siloxanes needs to be kept below 1 ppm in order to avoid damages.

Adsorption on high-surface area materials, namely silica gel, zeolites and activated carbons, is a well-assessed method for siloxanes removal (Mona, 2009; Ajhar et al., 2010; Schweigkofler and Niessner, 2001; Matsui and Imamura, 2010; Lenntech, XXXX; Ricaurte Ortega and Subrenat, 2009; Finocchio et al., 2009; Sorenau et al., 2011). They act as adsorbents, and the pollutant is trapped through a physical interaction with the surface. Their principal characteristic is consequently the very large internal surface (500–1500 m^2/g), split between macropores (pore diameter >20 nm) and micropores (<20 nm). Since the work of Schweigkofler and Niessner (2001), who first identified activated carbons and silica gel as promising adsorbents for siloxane removal, several works, particularly in the past 5 years, have explored the same methods or proposed different approaches, as biological removing (Popat and Deshusses, 2008; Accettola et al., 2008) or deep chilling (Ajhar et al., 2010). Due to the contemporary presence of siloxanes and hydrogen sulfide in a biogas stream, the purpose of the present work is to check which, among a set of commercial high-surface area materials already studied for H_2S removal, can be efficiently used to reduce siloxanes concentration down to less than 1 ppm. The removal action and the mechanism involved were studied by

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forcing a L2 contaminated nitrogen stream through a cylindrical reactor filled with the selected adsorbent powder at different operative parameters. The regeneration process, namely the possibility to return, through an in situ desorption, to the primary state of the activated carbon, has been tested. Accordingly the capacity loss due to the regeneration process was quantified. A thermal process ($T > 200\ °C$) was attempted in the earlier papers to achieve the complete desorption of pollutants from saturated ACs and regenerate them for a successive use (Schweigkofler and Niessner, 2001; Accettola et al., 2008). Successive studies (Sorenau et al., 2011) assessed a 5–25% loss in adsorption capacity after the regeneration process regarding silica compounds and hydrogen sulphide; a complete regeneration can be achieved only for volatile organic compounds (VOC). Finocchio et al. (2009) discovered that regeneration is only partial due to the formation of non-volatile compounds on the ACs surface. The impossibility to regenerate the spent carbon rises considerably its cost as purification system (Dewil et al., 2006; Wheless and Pierce, 2004), otherwise very low. Adsorbent beds have to be replaced regularly avoiding a continuous process (or forcing parallel adsorbing beds systems).

Different commercially available activated carbons, with a different functionalizing processes, different specific surface areas and different pH values were tested and their performances as siloxane removal agent compared. Furthermore two different zeolites and a silica gel powder were tested. The final aim of the investigation is to find if the same material could be efficiently used for both siloxane and hydrogen sulfide and to which extent the presence of siloxane influences the up take of hydrogen sulfide. The first step of this activity produced the list of adsorbents, namely granular activated carbons (Monteleone et al., 2011); the second step, reported in the present paper, looks at siloxane removal; a third step will be the simultaneous contaminant removal study from a real biogas.

Among the different siloxanes, all with boiling point above 100 °C, the L2, chemical formula Si2O(CH3)6, has been selected for its greater volatility; we assumed, as already observed (Ricaurte Ortega, 2009), that siloxanes with lower volatility and higher molecular mass can be removed easier than L2. Considering that siloxanes removal was established as an interaction of organic radical bonded to the Si with the carbon surface, the affinity of L2 with the other siloxanes, both linear and cyclic, is supposed to generate qualitatively similar results.

Moreover tanks with certified percentages of L2 in nitrogen are commercially available, allowing direct and accurate calibration; the same is not available for heavier siloxanes.

2. Samples

Five different commercial activated carbons (AC) were tested. Their performances are compared to understand which mechanism controls siloxane removal and which carbon characteristic plays role in the adsorption process. The carbons were sieved to get 250–350 micron powder mesh. The effect of a slightly different mesh (350–700 μm) has been tested but no significant effects on results were observed. Samples differ in specific area surfaces (split between micropores and macropores) and in the activation process undergone, which made the surface either basic or acid or neutral. The samples, about 150 mg or 300 mg carbon powder, were weighed before the test. Table 1 summarizes data of the tested activated carbons; for each carbon the activation elements (factory impregnation) and the specific surface area from BET (Brunauer–Emmett–Teller) measurements on primary samples (performed in ENEA, the Italian National Agency for New Technologies, Energy and Sustainable Economic Development) are reported.

Table 1
Characteristics of the tested activated carbon.

Activated carbon	Impregnant	Specific area ($m^2\,g^{-1}$)
AC1	Cu Cr Salt	978
AC2	KOH	691
AC5	KI	880
AC3	Virgin, basic	923
AC7	Virgin, acid	1100

Apart from the carbons, two different commercial zeolites and a silica gel powder were tested.

3. Experimental

Fig. 1 shows the scheme of the adsorption measurement apparatus. A nitrogen flow containing a defined percentage of L2 enters a 6 mm quartz tube (reactor R in Fig. 1) passing through an inert septum fixed at half reactor height entirely covered by the adsorbent powder under test, typically 150 mg or 300 mg.

The L2 over N2 volume ratio is obtained by opportunely mixing two nitrogen flows coming from a cylinder (Air Liquide, 99.9%): the first flow, F1, bubbles in a bottle filled with liquid L2 (S). The stream, enriched with the vaporized L2, is then mixed and diluted with the F2 stream. The F1 and F2 flows are controlled by the two Thermal mass flow controllers, MFC1 (Bronkhorst 0–1 mL/min) and MFC2 (Bronkhorst 0–100 mL/min). While the F2 flow rate was set at its maximum value, the F1 one was varied (0.5–3 mL/min) according to the requested L2 concentration level. With this mixing set up the available and stable concentration range obtainable, after a stabilizing period of a couple of hour, was between 20 and 300 ppm of L2. The system was previously calibrated by a L2-in-N2 calibrated cylinder as feed gas.

After mixing, the stream is sent to the adsorbing bed and then to the outlet. The exiting L2 + N2 is automatically and periodically (every 6 min) sent to the detector, a Perkin Elmer Mass Spectrometer Mod. Clarus 580, equipped with an inlet valve allowing "in line" measurements.

A preliminary measurement was carried out on the input stream (by-passing the reactor) before each test in order to check and adjust the L2 concentration level and ensure its constant trend.

Adsorption measurements were carried out at 30 °C. A PID (proportional–integral–derivative) thermo-controlled heating sleeve placed around the reactor was used for regeneration tests to drive the L2 desorption of the activated carbon (AC). The chemical analysis of the stream at the reactor outlet is measured by the 580 GC-MS Perkin Elmer spectrometer, calibrated with a 100 mL/min flow from a certified 100 ppm L2 in nitrogen tank (Air Liquide). The mass spectrometer, equipped with a multi-port inlet automated valve, is in-line with the rector. A 100 μL sample of the gas coming out from the reactor is periodically (every 6–8 min) sent to the spectrometer and analyzed.

The Mass Spectrometer (MS) analysis parameters were: Source Temperature: 200 °C, mass scan: 30–300 amu.

The presence of residual L2 is detected by the mass 147 fragment (Fig. 2). This fragment is specific of L2 and is produced when the CH_3 group -Si bond has been broken; it is therefore the mass that uniquely characterizes and quantifies the presence of L2.

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Fig. 2 shows a typical spectrum when a L2-in-N2 stream gas is sent directly to the spectrometer inlet valve. The mass spectrum range is limited to masses higher than 30 amu, to avoid the signal being normalized to the nitrogen peak (at 28 amu), predominant with respect to every other peak.