



Facultat de Ciències

Memòria del Treball Final de Grau

Siloxane transformation reactions by means of activated carbon towards biological availability

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Data de dipòsit de la memòria a secretaria de coordinació:

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Abstract

Siloxanes are silicon based compounds that are present in biogas. The need for new and better ways to obtain renewable energy is incrementing. The biogas produced in landfills and wastewater treatment plants can be used as a renewable energy source, however in all of the possible utilizations the siloxane removal is necessary. The costs of siloxane removal nowadays are high and not a cost effective solution has come yet. The biological removal of this compounds is a possibility currently under research, but the low solubility in water that siloxanes present is a problem. The investigation in order to make the siloxanes more bioavailable is necessary, and this study goes in that direction.

A total of 4 commercial activated carbons (ACs) have been tested for the absorption and partition of the octamethylcyclotrisiloxane (D4) in batch experiments using different humidity conditions. The ACs tested present different physical and chemical properties, given by their different activation processes: ones were activated with steam and others with H_3PO_4 . Siloxane partition into gas-water-AC phases was studied. The end goal was to prove the capacity of the ACs to catalyze the ring-opening of D4 to transform it into more soluble compounds, which may be more accessible to microorganisms to remove it biologically.

All the ACs tested adsorbed the D4 completely in dry conditions. The results showed that the recovery of D4 by hexane extraction from the AC matrix was low due to the potential transformation of the D4 into other compounds either not extractable or nor detectable by the analytical methods used. When the conditions of humidity were higher, the results showed that the ACs adsorbed less D4: a little amount remained in the gas phase.

A chemically AC was selected because it was the best performing AC at D4 removal and transformation. Extraction was made with a polar solvent, so the presence of silanediols could be detected. Silanediols are water-soluble by-products from siloxane hydrolysis, thus making the formation of silanediols the path to follow in future biological removal of siloxanes technologies.

Resum

Els siloxans són compostos derivats de la silicona presents en el biogas. La necessitat per a millors i noves maneres de obtenir fonts d'energia renovables està augmentant. El biogas generat a abocadors i plantes de tractament d'aigües residuals pot ser utilitzat com a una font d'energia renovable, però en tots els seus possibles usos l'eliminació de siloxans és necessària. El cost de la eliminació dels siloxans actualment és alt i encara no ha sorgit cap solució rentable al mercat. L'eliminació biològica d'aquests compostos és una possibilitat que actualment està sota recerca, però la baixa solubilitat en aigua que presenten els siloxans és un problema. La investigació per tal de fer els siloxans més biològicament accessibles és necessària, i aquest estudi va en aquesta direcció.

Un total de 4 carbons activats (ACs) comercials han estat provats per la adsorció i partició de octametilciclotrisiloxà (D4) en experiments en discontinu utilitzant diferents condicions d'humitat. Els ACs provats presenten diferents propietats, tant físiques com químiques, donades per els seus diferents processos d'activació: uns han estat activats amb vapor i altres amb H_3PO_4 . La partició dels siloxans en les fases gas, aigua i AC ha estat estudiada. El objectiu final és demostrar la capacitat dels ACs de catalitzar la obertura dels anells del D4 i transformar-lo a compostos més solubles, això podria fer-los més accessibles per els microorganismes per tal de eliminar-los de manera biològica.

Tots els ACs utilitzats han adsorbit el D4 completament sense la presència d'humitat. Els resultats mostren que la recuperació del D4 amb extraccions amb hexà és baixa degut a la potencial transformació que pateix el D4 cap a compostos no extraïbles o no detectables per els mètodes analítics utilitzats. Quan les condicions d'humitat són altes, els resultats mostren que els ACs adsorbeixen menys D4, una mica es queda a la fase gas.

S'ha seleccionat un AC activat químicament (H_3PO_4) ja que ha estat el AC que millor ha realitzat la eliminació i transformació del D4. L'extracció ha estat realitzada amb un dissolvent polar, per tal de detectar la presència de silanediols. Els silanediols són uns compostos solubles en aigua, derivats de la hidròlisi dels siloxans, fent així la formació de silanediols el camí a seguir en les investigacions de tecnologies de eliminació biològica dels siloxans.

Resumen

Los siloxanos son compuestos derivados de la silicona, presentes en el biogás. La necesidad de mejores y nuevas maneras de obtener fuentes de energía renovables esta aumentando. El biogás generado en los vertederos y plantas de tratamiento de aguas residuales puede ser utilizado como una fuente de energía renovable, pero en todos sus posibles usos la eliminación de los siloxanos es necesaria. El coste de la eliminación de los siloxanos es alto y actualmente aún no ha surgido ninguna solución rentable en el mercado. La eliminación biológica de estos compuestos es una posibilidad que actualmente está siendo investigada, pero la baja solubilidad de los siloxanos en agua es un problema. La investigación para hacer de los siloxanos un compuesto más biológicamente accesible es necesaria, y este trabajo va en esta dirección.

Un total de 4 carbones activos (ACs) comerciales han sido utilizados para la adsorción y partición de octametilciclotrisiloxano (D4) en experimentos en discontinuo utilizando diferentes condiciones de humedad. Los ACs probados presentan diferentes propiedades, tanto físicas como químicas, dadas por sus diferentes procesos de activación: unos han sido activados con vapor y otros con H_3PO_4 . La partición de los siloxanos en las fases gas, agua y AC han sido estudiadas. El objetivo final es demostrar la capacidad de los ACs de catalizar apertura de los anillos del D4 y transformarlo a compuestos más solubles, haciéndolos así más accesibles para los microorganismos en aras de ser eliminados de manera biológica.

Todos los ACs utilizados han adsorbido el D4 completamente en ausencia de humedad. Los resultados muestran que la recuperación del D4 en extracciones con hexano es baja, debido a la potencial transformación que sufre el D4 hacia compuestos o no extraíbles o no detectables por nuestro método analítico. Cuando las condiciones de humedad son altas, los resultados muestran que los ACs adsorben menos D4, un poco se queda en la fase gas.

Un AC activado químicamente (H_3PO_4) ha sido seleccionado dado que ha sido el AC que mejor ha realizado la eliminación y transformación del D4. La extracción ha sido realizada con un disolvente polar, para poder detectar la presencia de silanedioles. Los silanedioles son unos compuestos solubles en agua, derivados de la hidrólisis de los siloxanos, haciendo así la formación de silanedioles el camino a seguir en las investigaciones de tecnologías de eliminación biológica de siloxanos.

1. Introduction

1.1 Biogas

Biogas is produced during the anaerobic digestion of organic material, following these four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Figure 1) [1]. The biological aspects and parameters of the process are discussed in specialized literature [2] [3].

1. Hydrolysis: in the first step the insoluble organic materials and the high molecular compounds are digested into organic soluble substances.
2. Acidogenesis: in this step, the components digested during the hydrolysis are further degraded into acetic acid, volatile fatty acids, H_2 and CO_2 .
3. Acetogenesis: the higher organics alcohols and acids produced by the acidogenesis are transformed into mainly acetic acid and also CO_2 and H_2 .
4. Methanogenesis: all of the byproducts generated in the third phase are now digested into methane and carbon dioxide.

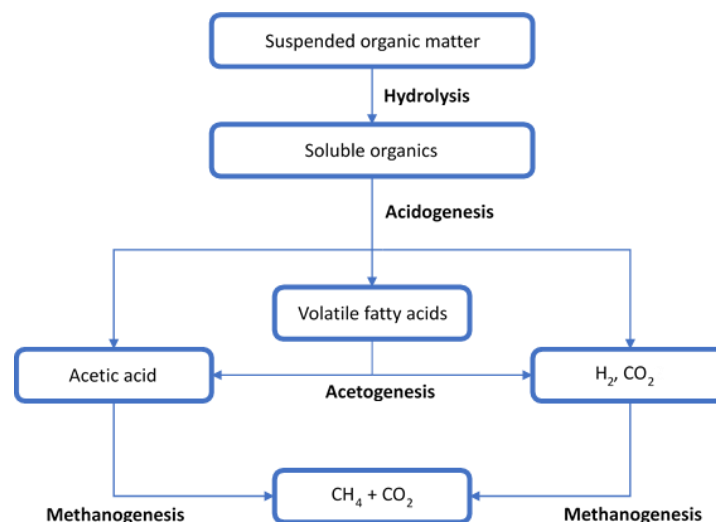


Figure 1. Process of the anaerobic digestion and biogas formation [1].

The biogas produced during the anaerobic digestion both in wastewater treatment plants (WWTP) and landfills is generally used in energy production. In some countries, methane-rich gas from landfills is burned or used for energy production. Due to the increasing interest in renewable sources of energy, biogas has become an alternative to conventional fuels. Biomethane upgraded from biogas is also being used as vehicle fuel in some countries [4].

The composition of biogas (Table 1) depends on the origin of the residue digested. Its composition may differ if biogas comes from landfill or anaerobic digestion of sewage sludge [5].

Table 1. Composition of landfill and anaerobic digester biogas [1].

Component	Unit	Landfill	Sewage sludge
CH ₄	vol%	35-65	53-70
CO ₂	vol%	15-50	30-47
N ₂	vol%	5-40	0-3
H ₂ O	vol%	0-5	5-10
O ₂	vol%	0-5	0-1
H ₂	vol%	0-3	-
CO	vol%	0-3	-
H ₂ S	ppm	0-100	0-10000
NH ₃	ppm	0-5	0-100
Cl ⁻	mg/ Nm ³	20-200	0-5
VOC	mg/m ³	0-4500	-
Siloxanes	mg/m ³	0-50	0-41

1.2 Biogas as a renewable energy source

Biogas is a source of energy with significant environmental benefits. It is a renewable energy source, but nowadays according to Red Eléctrica Española [6], in Spain only 40.8% of the electrical demand is provided by renewable sources. Thus, it is necessary to search ways to increase their share in the market [7].

In the year 2007 the principal producers of biogas in the European Union are (in Mtep): Germany 2.38, United Kingdom 1.62, Italy 0.41, Spain 0.33, France 0.31 and the Netherlands 0.17 [8]. Also, according to EBA 2015 [9], there were 17240 biogas plants in Europe in 2014, with a total capacity installed of 8339 electrical MW. Biogas production in Europe accounted for 13.4 million tons of oil equivalent (10% increase compared to 2012), which represented 52.3 TWh of electricity produced and net heat sales to heating district networks of 432 megatons of oil equivalent [5]. In more recent years, the production of energy from biogas in the European Union, has grown and it is showed in Table 2 [10].

Table 2. Primary energy production of biogas in the principal countries in the European Union in 2012 (in ktoe) [10]

Country	Landfill gas	Sewage sludge gas	Other biogas
Germany	123.7	372.1	5920.4
United Kingdom	1533.9	269.7	0
Italy	37.6	42	766.1
Czech Republic	31.7	39.4	303.8
France	279.1	79.6	53.3
Netherlands	29.9	53.1	214.5
Spain	140.8	33.8	116.2

As it can be seen in the Table 1, biogas composition can be different and also its calorific potential, which is determined by the methane concentration. The heating value of biogas is expressed as the energy released when 1 Nm³ of biogas is combusted [1]. The heating value of biogas depends on the source (landfill or digester). In the case of the landfill for every m³ of

biogas 4.4 kWh of electric energy can be produced, and 1 m³ of biogas obtained during anaerobic digestion can produce 6.5 kWh of electric energy [1].

1.2.1 Biogas as fuel for boilers and stoves

Biogas can be used as an alternative to natural gas, although it has to match the standards. In order to replace the natural gas from the boilers and stoves, biogas has to be around 100% pure, if not, natural gas (at 20 mbar) has more heating value. Biomethane can have a lower concentration of methane (93%), but it must have a higher pressure than 20 mbar that the normal stoves work. H₂S has to be lower than 10 ppm in the stream, or it can have corrosive impacts and toxicity [11]. Boilers tolerate less methane purity in the gas stream, also the removal of H₂S is not necessary in large boilers. Generally speaking, biogas used in boilers must have H₂S below 250 ppm in order to avoid excessive corrosion and deterioration of the lubrication oil [12].

1.2.2 Fuel for engines and gas turbines for producing electricity

For a normal function of the engines a 35% of CH₄ in biogas stream is needed. Common energy plants have a production capacity of 5 MW or more, but an ordinary biogas plant cannot give enough fuel for the engine to work in a constant flow.

For this technology, concentration of H₂S can be up to 200-1000 ppm, so the H₂S will not limit the combustion reactions. During combustion reactions, siloxanes are transformed into microcrystal silica that deposits into engines and turbines causing erosion, therefore siloxanes must be removed. The water presence has to be reduced as low as possible to avoid the risk of wet compression of fuel gas [11].

1.2.3 Injection into the natural gas grid

Another utilization possibility of biogas is the injection into the natural gas grid. In order to be injected into the grid, biogas has to be upgraded into the standards of the natural gas, according to the European Commission (*Table 3*). Depending on the composition of biogas one technique of upgrading or another ends up being the most suitable [11].

Table 3. Standards for gas quality in the natural grid in EU and USA

Parameter	Unit	EU	USA
Minimum CH ₄	(% mol)	70-98	93.5-95.5
Maximum CH ₄	(% mol)	1-8	2-3
Maximum O ₂	(% mol)	0.01-1	0.2-3
Maximum N ₂	(% mol)	2-10	-
Maximum H ₂	(% mol)	0.1	0.1
Maximum H ₂ S	mg/m ³	2-15	6-88
Maximum total sulfur	mg/m ³	10-150	265
Water content	g/m ³	0.05-1	65

1.2.4 Fuel for vehicles

Using upgraded biogas as vehicle fuel is a possibility of increasing interest worldwide. According to E.ON [13] a large energy company from Sweden, the requirements in order to inject biomethane as vehicle fuel are specified in Table 4.

Table 4. Standards for gas quality as vehicle fuel, according to E-ON 2011

Parameter	Unit	E.ON
Minimum CH ₄	(% mol)	>96
Maximum CH ₄	(% mol)	3
Maximum O ₂	(% mol)	1
Maximum N ₂	(% mol)	5
Maximum H ₂	(% mol)	4
Maximum H ₂ S	mg/m ³	5

Due to the requirement of high CH₄ purity, chemical absorption and cryogenic separation are candidate technologies for biogas upgrading. H₂S removal is also required.

1.3 Biogas upgrading

In order to increase the calorific value and to remove undesired components from the biogas, it is necessary an upgrading process. The objective of this process is to increase the percentage of methane in the biogas, so that the biogas is methane-rich, and also to remove harmful compounds such as H₂S or siloxanes. The future of the utilization of the biogas as an energy source goes through making its upgrading easier and more cost effective. The most common techniques for biogas upgrading are described in the following sections.

1.3.1 Water scrubbing and physical absorption

Water scrubbing is used to remove CO₂ from the biogas, due to its higher solubility than methane. With this process it is possible to also remove H₂S, but it can cause corrosion into the equipment, thus making it necessary to remove it in prior stages [5]. With this process the biogas obtained contains 80-99% of methane composition. The physical absorption instead of water uses organic solvents to absorb the CO₂ in the gas. This process has the limitations that cannot separate N₂ and O₂ from the gas stream, and also the H₂S has to be removed prior to the physical absorption [11].

1.3.2 Cryogenic separation

Given the different condensing temperatures of CO₂ and CH₄, these compounds can be separated with condensation processes. This process allows the separation of the CO₂ from the methane and also separate O₂ and N₂. Cryogenic separation presents a loss of CH₄ concentration of 1%, thus making it a great technology [11].

1.3.3 Chemical absorption

Chemical absorption consists in the incorporation of a solvent that can react with the CO₂ of biogas. This technique is very selective because the solvents used only react to the CO₂ so the methane would not interact with the solvent and there are no CH₄ losses. The limitation of this process is the recovery of the solvent, that requires great energy consumption and heat in order to regenerate the chemical solvents[11].

1.3.4 Membrane separation

Membrane separation is an easy process and has a low cost. The process consists in the separation through a membrane of the components of the biogas in a molecular level. The membranes more commonly used are polyimide and cellulose acetate-based. CO₂ and H₂S can be removed from the biogas stream but the membrane can also let through some molecules of methane, so in order to obtain a methane rich biogas, the losses of methane are considered to be high [11].

1.3.5 Pressure swing adsorption

Pressure swing adsorption (PSA) processes are based on the mechanism that gas molecules can be selectively adsorbed to solid surfaces according to their molecular sizes. PSA can separate CH₄ from N₂, O₂, and also H₂S. The concentration of CH₄ after upgrading is typically about 96–98% and CH₄ losses are about 2–4%.

1.3.6 Biological upgrading

Methanobacterium thermoautotrophicum is a methanogen chemo-autotrophic bacteria that produces methane into the gas stream, thus incrementing its CH₄ concentration. Using *M. thermoautotrophicum* can increase the concentration of biogas from 60% to 96%, while H₂ and H₂S are not detectable

1.4 Siloxane occurrence and removal

Siloxanes are a subgroup of silicones containing Si-O bonds with organic chains, such as: methyl, ethyl or other functional groups, bonded to the silicon atom [14]. The sources of siloxanes are increasing over the last years. Methylsiloxane solvents are used because they are aroma-free, nontoxic and they are exempt of volatile organic compound regulations. Their low-surface tension and water-repelling properties make them a perfect component in all kind of personal care products, such as cosmetics, detergents, deodorants, shampoos and hairsprays; they are also present in other pharmaceutical compounds. Their presence in the market has increased in the last 15 years [14].

During the combustion of biogas, the organic silicon compounds present are oxidized into microcrystalline silicon dioxide, which is similar in both physical and chemical properties as glass. This microcrystalline silicon dioxide can deposit in the engine parts thus producing abrasion and if not removed can produce irreversible damage on the engine or one of its parts. It can also deactivate the surface of the catalyst that operates as an emission control, or even can end up in the engine oil making its replacement mandatory [4].

The operating costs are rising due to all these negative effects. The need to install gas purification systems or removing the deposits of microcrystalline silicon dioxide, with the increment maintenance and costs of the operation cost, is a problem that the plants operators are facing nowadays [15].

The siloxanes can be volatile, and are low molecular weight organosilicon fluids with high vapor pressure at ambient conditions. The structure of a siloxane can be linear and cyclic. Only L2 and D3 are considered to have a slightly water solubility and a vapor pressure high enough (*Table 5*).

Table 5. Chemical properties of siloxanes founded in a digester gas [4]

Compound	Abbreviation	Molecular Weight (g mol ⁻¹)	Water solubility at 25°C (mg L ⁻¹)	Vapor pressure at 25°C (kPa)
Trimethyl silanol	TMS	-	35	2.13
Hexamethyldisiloxane	L2	162	0.93	4.12
Octamethyltrisiloxane	L3	236	0.035	0.52
Decamethyltetrasiloxane	L4	310	-	0.07
Dodecamethylpentasiloxane	L5	384	-	0.009
Hexamethylpentasiloxane	D3	222	1.56	1.14
Octamethylcyclotrisiloxane	D4	297	0.056	0.13
Decamethylcyclopentasiloxane	D5	371	0.017	0.02
Dodecamethylcyclohexasiloxane	D6	445	0.005	0.003

1.4.1 Commercially available siloxane removal technologies

1.4.1.1 Adsorption

The most widely used method to reduce the concentration of siloxanes is adsorption on activated carbon (AC) [15]. Silicon removal has been reported to happen in concentrations below 0.1 mg_{Si}/m³. Other authors have demonstrate that the depending on the AC that is used the siloxane removal can be quite different, so we have to take into account the BET surface area and the pore volume of the adsorbents [15].

The ACs are considered an universal adsorbent because of his low specificity in a retention process [16], his great capacity to retain compounds provokes a competitive adsorption of contaminants, since a biogas stream presents a broad range of different compounds (e.g., sulfur-containing, halogenated compounds or non-volatile) with concentrations with several orders of magnitude of difference [17].

To eliminate the other compounds that can be a limitation in the siloxane removal, the use of impregnated activated carbon is more effective. First, the sulfide compounds are removed, and then in a second stage with unimpregnated carbon is used to remove the siloxane. In this matter, the use of biotrickling filters is an alternative to impregnated carbon that could be more cost-effective [15].

Other adsorbent that is not widely used, but is promising are the Zeolites. According to other studies zeolites have shown great potential in the elimination siloxanes in a gas steam. Also have shown potential in the capacity of breaking the bonds of the siloxane molecule and thus forming silanediols, a by-product of the siloxane that is more soluble in water [18].

1.4.1.2 Absorption

There are two types of absorption: chemical and physical. In one hand chemical absorption is applicable to siloxane removal, these compounds are eliminated by the use of strong bases and acids. However, the application of the chemical absorption presents some inconveniences: corrosion is likely to happen [19], therefore an increment in the overall operation costs occurs. Moreover, if the siloxanes are eliminated by bases, it is highly probable to produce precipitates from carbonates, making similar erosion as the siloxane in the engines [17].

In the other hand, there is absorption by physical absorbents such as mineral oil, organic solvents or water. Physical absorption is mostly used in the context of siloxane analytics. Some solvents that can absorb the siloxanes are: methanol, hexane, acetone, tetrahydrofuran (THF) [15].

1.4.1.3 Deep chilling

This process consists in submitting the biogas to temperatures low as -70°C in order to condensate the siloxanes. If the siloxanes are condensed, they disappear from the gas stream and go to the water matrix. The more volatile siloxanes (e.g., L2, D3 and L3) cannot be condensed to decrease their concentration low enough. In order to obtain a reasonable decrease in the concentration of L4, D4 and D5, as low as $1\text{ mg}/\text{Nm}^3$, the temperature has to go between -55 and 70°C [15]. Due to the high investment and operation costs, this technology is only applicable at a higher flow rate, or in streams with a high concentration of siloxanes [15].

1.4.2 Siloxane removal technologies under development

1.4.2.1 Membrane separation

This technology uses dense polymeric membrane material that lets the siloxane go through the membrane and retain the methane rich gas. In other studies [15], 80% elimination of the siloxanes in the gas stream were found. The problem with this technology is that the operation costs are high, this is because the vacuum pumps and compressors need to create enough partial pressure in the system, and this requires energy.

1.4.2.2 Biological removal

The possibility of siloxane removal by anaerobic and aerobic biotrickling filters was tested by [20]. These authors used the siloxane as the sole carbon and energy source of the microorganisms. The problem with this technology is that the siloxane are not soluble, so it is hard for them to be incorporated for the microorganisms in the biotrickling.

Biodegradation technologies may reduce investment and operating costs, increment treatment capacities and require low energy and chemicals. Biodegradation technologies are difficult to implement in the elimination of siloxanes due to their low solubility and complex structure. The implementation of a technology that allows the siloxane to be bioavailable for the microorganisms is the next step into the siloxane removal.

In this study is proposed a biological treatment supported by activated carbon. The activated carbon would act as a catalyzer of the siloxanes [21] and thus produce silanediols, a more soluble compound that the microorganism could use as his carbon font.

1.5 Activated Carbons

AC is a material created in the industry in order to obtain a product with a high intern surface. This high intern surface makes AC a great adsorbent of a wide range of compounds, in dissolution or in gas phase. The high retaining capacity of the AC is due to his surface area and the size of the pores: micropores (size inferior of 2nm) confer to the AC high surface area, while mesopores (size between 2-50 nm) and macropores (size bigger than 50 nm) enable the AC to retain high molecular weight compounds [16].

1.5.1 Formation and activation

ACs are formed by the combustion or thermal decomposition of high carbon substances at below 800 °C of temperature in an inert atmosphere. Then the carbon product is activated in order to increase their porosity [22]. The properties of the product depend on the raw material, the activating agent and the carbonization processes. Almost all materials with high carbon content can be used, but the more common are: anthracite, lignite, coal and wood.

During the carbonization, the non-carbon elements and the residual carbon group into aromatic sheets, that leaves spaces that rises the pores of the carbon. The pore capacity is enhanced during the activation process. The activation is the process that creates further porosity and modifies the carbon surface. The activation can be done with carbon dioxide, steam or a mix of those gases, or can be activated with chemical agents such as H_3PO_4 , H_2SO_4 , HNO_3 , KOH [23].

The ACs present oxygen functional groups that modify the surface properties of the activated carbons, by adding wettability, polarity and acidity characteristics, and physico-chemical properties like catalytic and chemical reactivity [22].

1.5.2 Catalytic potential

According to [14] the oxygen functional groups that are located in the AC surface act as a catalyst to break the cyclic structure of siloxanes. The radicals situated on the surface of the AC are the ones that may have the potential to interact with the siloxanes and break and partition them. The ACs activated with chemical agents have showed to be more likely to interact and partition the siloxanes.

The oxygen functional groups on the activated carbon, as depicted in Figure 2, can be quantified with a method called Thermal programmed desorption (TPD). This method is used to measure the amount of oxygen functional groups that can act as a acid in the surface of the AC. The carbons that showed a major amount of carboxylic groups in the TPD tests are the ones that have major acids in his surface. The amount of acids presents in the surface have been linked to the catalytic potential of the AC in the D4 partition into other by-products [22].

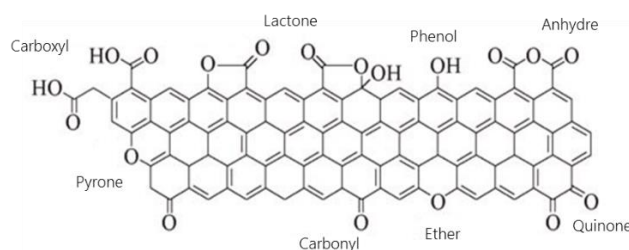


Figure 2. Oxygen functional groups in AC surface.

2. Ethical and Sustainability criteria

This study aims to give more data to further biotrickling investigations. In this context, the objective of the present study is to give more possibilities to the biological removal of the siloxanes, thus giving the energy recovery and utilization of biogas a more cost effective solution. The utilization of biogas as renewable energy source is a must in order to reduce the CH₄ and CO₂ global emissions and to obtain a future with more renewable energy sources.

This study was done reducing to a minimum the wastes and their toxicity. All the tests and preparations were carried under the gas extractor, with the use of gloves and protection glasses. The results of this study are original and no plagiarism was made.

3. Objectives

The siloxanes are non-soluble compounds that can be hardly transferred to water phase. This project studies the D4 transformation reactions promoted by activated carbon during adsorption processes.

- The first objective of this study is to investigate the transformation that the cyclic siloxanes (D4) present in biogas suffer in contact with activated carbons.
- Steam-AC and H_3PO_4 -AC are compared in terms of catalytic activity towards D4 transformation.

In order to fulfil the need for technologies that biologically remove the siloxanes, finding materials capable of transforming the siloxane into more soluble compounds is a must. This water soluble compounds should be available for the microorganisms to be biologically removed with a biotrickling filter.

- AC, which promote cyclic siloxane ring-opening reactions, are further tested in water-partition tests to study the changes in the by-products formed due to the water availability.

To identify the different siloxane by-products, different extraction and analytic methods were carried out. The different solvents allow to extract the different polar and apolar by-products.

- To compare the by-product distribution extracted and detected depending on the solvent used.

4. Material and methods

4.1 Activated Carbons

Four ACs were used for this study: RB3, Centaur, Silpure and Nuchar. All of the ACs were presented in pellet form. ACs were used in this form in order to extrapolate our results with other colleagues working in a Biotricking filter to also remove the siloxanes from biogas.

The textural and chemical characterization of the materials tested was previously performed by LEQUIA researchers. In table 4 the next textural properties of the ACs are specified: AC density, specific surface areas (S_{BET}), total microporous volumes (VDR_{N_2}), total pore volumes (V_t), mesopore volumes (V_{meso}), microporus volumes (VDR_{CO_2}).

Table 6. Textural properties of the AC considered and humidity content desorbed at 110°C

AC	ρ_{ap}	S_{BET}	VDR_{CO_2}	VDR_{N_2}	V_{meso}	V_t
[$cm^3 g^{-1}$]	[$g cm^{-3}$]	[$m^2 g^{-1}$]	[$cm^3 g^{-1}$]	[$cm^3 g^{-1}$]	[$cm^3 g^{-1}$]	[$cm^3 g^{-1}$]
Centaur	0.490	1070.3	0.305	0.425	0.107	0.532
Nuchar	0.240	2212.5	0.317	0.818	0.692	1.510
RB3	0.366	1274.6	0.367	0.495	0.084	0.579
Silpure	0.340	1812.0	0.345	0.682	0.197	0.879

According to previous studies a, textural properties described in Table 6 are good indicators in order to know if an AC is better than other retaining siloxanes. The total pore volume (V_t) is the property more directly linked to the adsorption capacity, also the S_{BET} and the V_{meso} have a correlation with the retention of siloxanes into the AC.

The chemical composition of the different ACs depends on the process of activation that they suffer. In the case of Nuchar and Silpure, they are activated with H_3PO_4 thus giving the AC more surface acidic sites. As shown in Table 7, Silpure and Nuchar present the higher quantity of evolved H_2O , CO and CO_2 in TPD analysis. The amount of oxygen functional groups may have a bigger role in the reactions of the AC with the siloxanes.

Table 7. Amount of H_2O , CO and CO_2 realized, obtained by integration of the areas under de TPD peaks of each AC and pH_{slurry} ,

AC	H_2O	CO	CO_2	pH_{slurry}
	[$\mu mol g^{-1}$]	[$\mu mol g^{-1}$]	[$\mu mol g^{-1}$]	[$\mu mol g^{-1}$]
Centaur	76	448	221	7.89
Nuchar	1841	2030	507	4.67
RB3	319	182	206	8.64
Silpure	2777	2049	579	6.51

4.2 Adsorption and partition tests

In order to study the partition that D4 suffers in contact with the mineral medium used for bacteria growth and the AC used to catalyze ring-opening reactions, adsorption and partition tests were carried out.

Previous studies have proved that silanediols and other forms of siloxanes appeared in contact with AC and D4 during adsorption tests [21] due to the humidity content of the ACs. The reduction on the D4 adsorption capacity of the ACs submerged in mineral medium and the partition between the three phases (gas, water (mineral medium) and AC) was also studied. The mineral medium used for bacteria growth has the composition shown in Table 8.

Table 8. Composition of the mineral medium

Compound	Concentration [g · L ⁻¹]
NaCl	0.5
MgSO ₄	0.1
CaCl ₂	0.01
NH ₄	0.02
NaNO ₃	1.0
KH ₂ PO ₄ ·H ₂ O	0.58
HEPES 10 nM	2.38

In order to study D4 transformation (Figure 3) we put 1 g of each AC in a 120 mL sealed bottle and 20 mL of mineral medium (Table 8), that acts as the water matrix. Once the bottle is hermetically sealed, 15 μ L of liquid D4 were incorporated. Then the samples are stirred for 48 hours to reach equilibrium between the D4 partition (Figure 3B):

- i) Remaining in the gas phase,
- ii) Solubilized in the water phase,
- iii) Adsorbed in the AC,
- iv) transformed into by-products remaining in the AC or solubilized in the water phase

Duplicates of every sample were made. Samples without water were made in order to compare the D4 adsorption and the by-products resulting without mineral medium (Figure 3A).

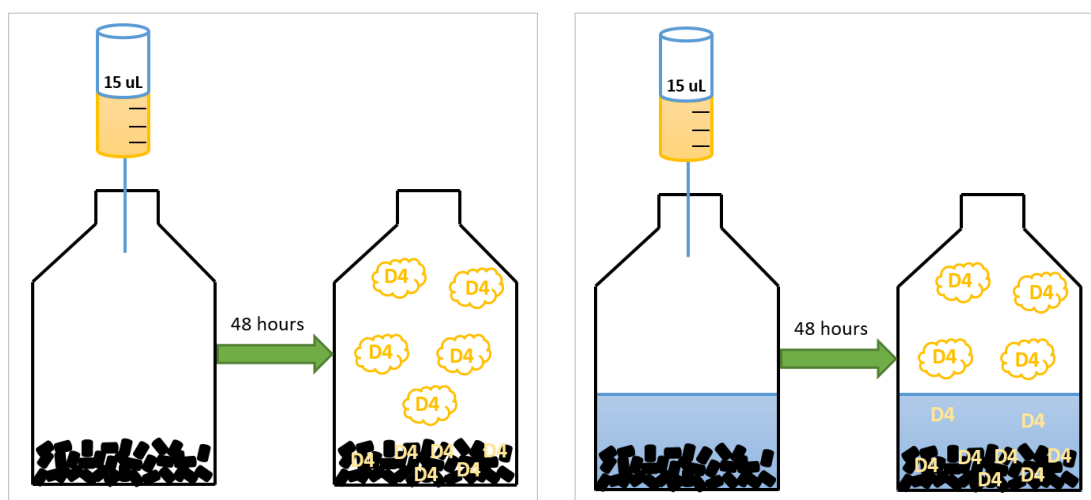


Figure 3. Left: diagram of D4 adsorption process (Section 5.2); Right: diagram of the D4 partition process between the gas, liquid and solid phases (Section 5.3-5.4).

4.3 Siloxane speciation analysis

4.3.1 GC-MS method for siloxane analysis

In order to analyze the D4 and the transformation products, two different solvents were used depending on the sample type and the polarity of the analysts, as shown in Table 9. Extraction techniques are show in the following sections.

Table 9. Extraction methods for siloxane analysis in the different equilibrium phases.

	Gas phase	Liquid phase	AC extraction
Solvent	Hexane	THF	Hexane / THF
Sample volume/mass	100 μ L	15 mL	1 g
Solvent volume	4 mL	3 mL	20 mL
Extraction method	Section 4.3.3	Section 4.3.4	Section 4.3.2

Depending on the solvent used, the GC-MS methods used for the analysis of siloxanes and silanediols are defined in Table 10.

Table 10. GC-MS method developed for siloxane quantification and silanediols identification.

Solvent	Hexane		THF	
	AC extraction	Gas phase	AC extraction	Water phase
Matrix				
GC-MS	Agilent technologies		Agilent technologies	
Model	7890A series GC/MSD		7890A series GC/MSD	
Capillary column	HP-5ms ultra inert		HP-5ms ultra inert	
Solvent delay	2.5 min		1.8 min	
Injector T ($^{\circ}$ C)	220		250	
Initial T ($^{\circ}$ C)	80		50	
T ramp	After 1 min of hold time, the initial temperature raises at 10 Kmin ⁻¹ until 110 $^{\circ}$ C. Then it raises to 260 $^{\circ}$ C at a rate of 25 Kmin ⁻¹ .		After 3 min of hold time, the initial temperature raises at 20Kmin ⁻¹ , with a hold time of 1 min. Then in raises up to 150 at a rate of 20 Kmin ⁻¹ . It reaches the end temperature at a rate of 50 Kmin ⁻¹ .	
End T ($^{\circ}$ C)	260		300	
Split ratio	1:10		1:20	

4.3.2 Extraction of D4 and by-products on the AC

For every sample a total of 1 g of the spent ACs was recovered after the tests, the water was removed in order to recover the maximum amount of AC possible, then the AC was mixed with 20 mL of hexane (Merck, 98%), mixed for 1 min in a vortex (IKA Vortex Genius 3) and stirred for half an hour (GFL 3005) at room temperature (22 \pm 1 $^{\circ}$ C) to extract the D4. The samples then have to be centrifuged (Hettich Zentrifugen, EBA 21) and filtered (0.2 μ m) so the hexane that contains D4 can be recovered.

ACs samples were treated with anhydrous tetrahydrofuran (THF) (Sigma-Aldrich, USA) in order to extract adsorbed siloxanes and potential polar transformation products that cannot be extracted using hexane. Samples of 1 g of AC were suspended in 20 mL of anhydrous THF, filtered, put in the vortex for 1 min and mixed for 30 min in an orbital mixer.

4.3.3 Gas phase siloxane analysis

The siloxanes in gas phase were analyzed by extracting 100 μ L of the gas from the headspace of the bottle and bubbled up into 4 mL of hexane in order to dilute the volatile compounds into the hexane.

4.3.4 Water phase siloxane analysis

For every sample 15 mL of mineral medium were recovered after our tests and was put with 3 mL of THF and 3.8 g of NaCl. The THF used in order to extract the silanediols and the siloxanes from the mineral medium. The NaCl was added in order to saturate the water and create a separation of phases between the THF and the water so the two compounds can be differentiated. Then the samples were mixed for 1 min in the vortex and then 30 min in an orbital mixer.

5. Results and discussion

5.1 Optimization of the siloxane and silanediols analytical procedure

Siloxanes were found using the different GC-MS method described Table 10. The different methods to identify the siloxanes, according to the capacity that they have to go through the column of the GC-MS. The separation between the different compounds give each one of the siloxanes a particular retention time in this particular test. The different retention times that siloxanes have are shown in Table 11.

The GC-MS analysis program allow to see the retention time of each compound and their analytical ions, so the identification of every siloxane was made according to their analytical ions (Table 11).

Table 11. Retention times and analytical ions of the cyclic siloxanes detected by hexane extraction of the AC and in the gas phase.

Compound	Analytical ions (m/z)	Retention time (min)
D4	133, 265, 281	3.91
D5	73, 267, 355	4.92
D6	147, 324, 341	6.34
D7	147, 415, 503	7.4
D8	147, 327, 401	8.26
D9	147, 355, 429	8.98

Silanediols identification was made according to the extraction with THF as a solvent, in order to see the more polar compounds presents in the samples. The retention times of the silanediols (Table 12) were found according to their analytical ions, that the GC-MS software provides. The retention times were experimental because with every GC-MS method can be different.

Table 12. Retention times and analytical ions of the silanediols detected by THF extraction of the AC and in the water phase extraction

Silanediols	MW (g mol ⁻¹)	Analytical ions (m/z)	Retention time (min)
Dimethylsilanediol	92.2	77/45	1.96
Tetramethyl-1,3-disiloxanediol	166.3	133/151	4.88
Hexamethyl-1,5-trisiloxanediol	240.5	207/191	6.94

5.2 D4 adsorption and transformation onto ACs

The results of the adsorption tests (Figure 4A) show a great absorption of the D4 into the AC. In this case all the gas samples showed a concentration of D4 below the detection limit of the GC-MS, therefore each AC adsorbed 14.34 mgD4/g AC.

When the samples of AC were analyzed by hexane extraction, RB3 showed the higher amount of extractable D4 (33%) and Nuchar the lower (5%). If the D4 was not present in the gas matrix and either at his totality in the AC matrix, it can be assumed that the siloxane has been transformed into other compounds (grey bars).

In Figure 4b the transformation of the D4 into other siloxane compounds is shown. RB3 and Centaur are the ACs that presented less transformation of the D4 into other siloxane compounds. Contrarily Nuchar and Silpure present a high transformation rate of the D4 into D5, D6 the most, and other siloxane compounds with more molecular weight (e.g., D7, D8, D9). Further D4 transformation may be to compounds i) non-extractable by hexane or ii) no detectable by the GC-MS method used.

The high transformation that D4 suffer in Silpure and Nuchar is given by the activation process that these carbons suffer. In the case of Silpure and Nuchar, both are activated by H_3PO_4 , giving them a high quantity of oxygen functional groups, as revealed by TPD analysis (Table 7). The chemical properties of these ACs shows that they are more likely to transform the D4 into other siloxanes. RB3 and Centaur are ACs activated by steam, so the presence of oxygen functional groups (CO , CO_2 and H_2O in TPD analysis, Table 7) is lower, making them less likely to produce transformation of the D4.

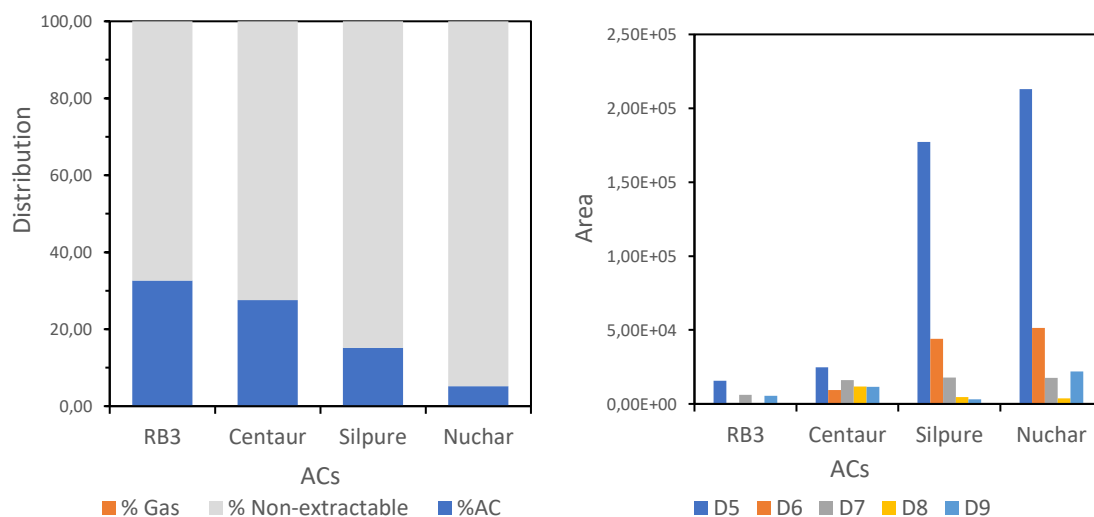


Figure 4. Left: D4 detected on gas phase, extracted of the AC and non-extractable; Right: D4 transformation products detected on the hexane extraction of the AC.

According to Cabrera-codony [14] the process of transformation of the siloxanes involves the acidic groups from the AC and the siloxane. This process needs the action of water molecules in order to function and to form new siloxanes that are not present, as we see in (Figure 5). ACs were used without a pre-drying step, therefore, they have some water adsorbed from the humidity of the air.

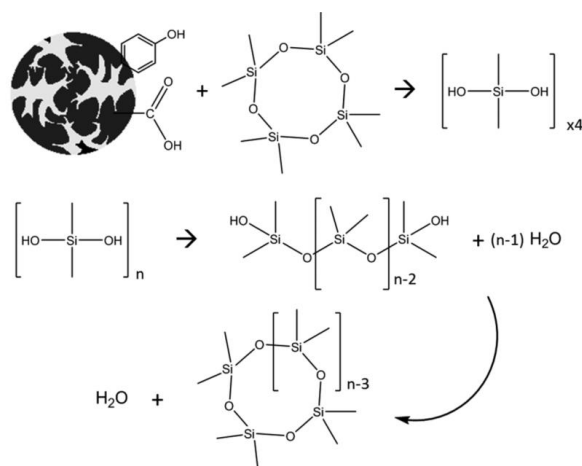


Figure 5. Process of siloxane transformation in presence of AC. Extracted from [22]

5.3 D4 water-partition in presence of AC

In the previous tests, transformation of the D4 into other siloxane compounds was found. In this test the partition of D4 in presence of water was studied.

The results showed a decrease in the adsorption capacity of the different ACs. Results showed a higher percentage of D4 present in the gas matrix, which previously (without water addition) was not detected. The presence of water seems to difficult the adsorption capacity of the different ACs tested since some D4 was detected in the gas phase (Figure 6A, orange bars).

Silpure and Nuchar presented a lower presence of D4 in the AC matrix by the hexane extraction. In the presence of water an increment on the catalyzation of the D4 into other compounds is showed, since this reaction require water (Figure 5). Centaur showed a drop in his D4 extracted, even though Centaur was not activated with H_3PO_4 . The drop in the D4 extraction of Centaur showed that the presence of water accelerates the reactions that the siloxanes suffer eventhough this AC have lower amount of acidic surface groups (Table 7).

In the partition analysis of the ACs samples (Figure 6B), only RB3 and Nuchar showed other siloxanes apart from D4 by hexane extraction. In Nuchar D5 and D6 were found, but not as much compounds as in the tests performed without water addition about more than one order of magnitud. Therefore, it can be concluded that the presence of water enhances the catalytic reactions to transform the D4 into more soluble compounds like silanediols [18], that cannot be detected by hexane extraction.

Thus, the extraction method with an apolar solvent (hexane) did not provide information about the soluble compounds either in the AC or the water matrix, so new tests with a more polar solvent (THF) were required.

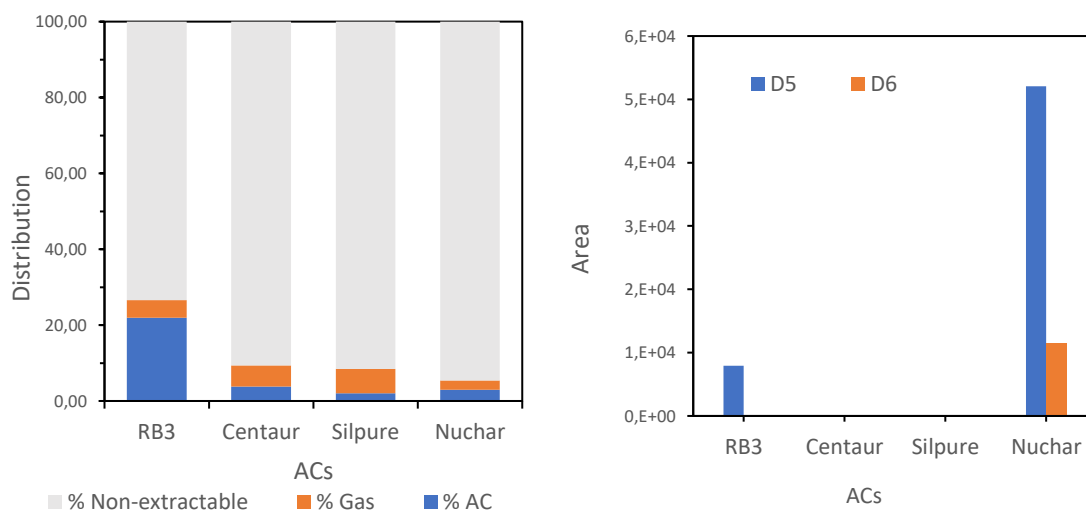


Figure 6. Left: D4 distribution between gas phase, extracted from the AC as D4 and transformation products; Right: D4 transformation products detected on the hexane extraction of the AC.

5.4 Silanediols analysis

The THF extraction tests were performed with RB3 and Nuchar. After new partition tests carried out like ones in 5.2 section, the extraction of the compounds on the AC was done using THF, a more polar solvent that can allow to recover the polar compounds that may be formed (silanediols). The results for RB3 analysis, either AC and water matrix, were not conclusive and the GC-MS was not able to identify the silanediols.

In the Nuchar test, silanediols were found both attached to the AC and in the water phase. The identification was done according to his retention time (Table 11). In the water matrix the only silanediol found was dimethylsilanediol (Figure 7A). Silanediols, in particular dimethylsilanediol are soluble in water [18], thus making it the only silanediol found in the matrix analysis.

In the AC analysis, the chromatogram shows more compounds. The presence of this compounds is due to their low solubility in water, they are not able to go to the water matrix. In Figure 7B, the partition of D4 is also visible as D3, D5 and D6 are still founded. In the AC analysis dimethylsilanediol, Tetramethyl-1,3-disiloxanediol and Hexamethyl-1,5-trisiloxanediol were found.

The presence of silanediols in the samples is due to the chemical properties of Nuchar, as is discussed in 5.2 and 5.3 section, this is because of the reactions siloxane-AC that happens in presence of water.

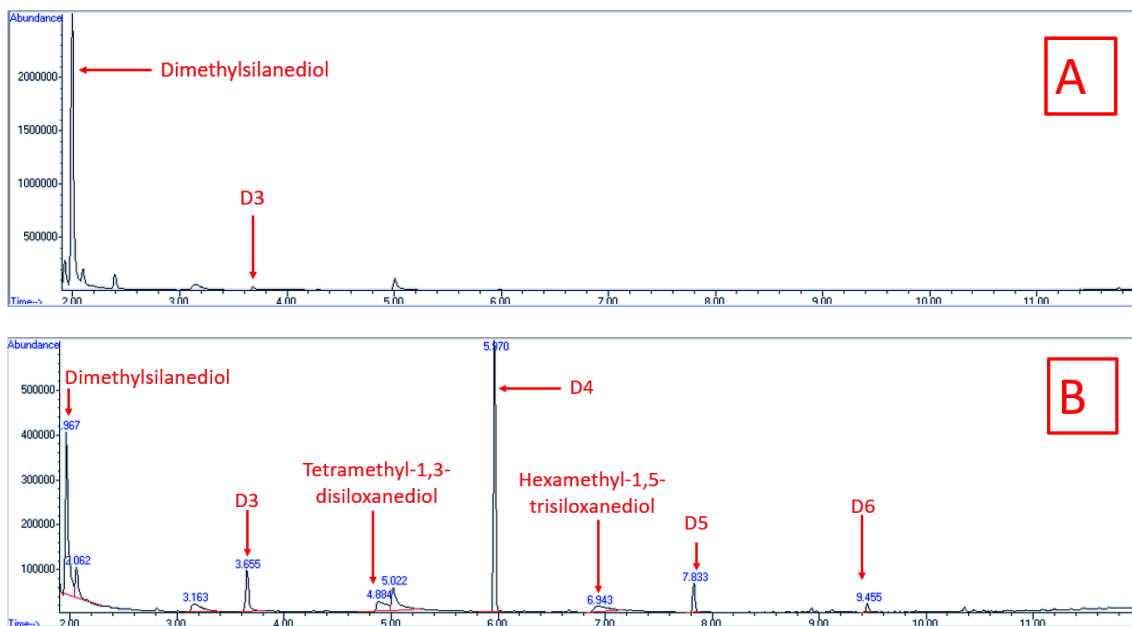


Figure 7. On the y axis is represented the area in the GC-MS, on the x axis the retention time. A) Chromatogram obtained in the analysis of the water matrix from Nuchar. B) Chromatogram obtained in the analysis of the Nuchar AC.

The next step to further the D4 partition into more soluble compounds would be to run the test for more than 48 hours, in order to see if the time is a factor in this reactions and to see if the increment of the concentration of silanediols is significant.

6. Conclusions

It has been studied the partition of the D4 in AC, both in dry conditions and in presence of mineral medium. The experimental results showed that in dry conditions the AC is able to adsorb completely the D4 injected into the system. However, the D4 adsorbed by the AC is only partially recovered by the hexane extraction. At the same time, other siloxanes like D5, D6, D7 were formed and extracted.

The ACs that had been activated by steam (RB3 and Centaur) did not show as much D4 transformation as the ACs that had been activated with H_3PO_4 (Silpure and Nuchar). H_3PO_4 -AC are the ones that most catalyzed D4 hydrolysis and condensation reactions to form other siloxanes by-products. The catalytic activity of Nuchar and Silpure is due to his chemical composition: the chemical activation process undergone provided the surface carbon oxygen functional groups which interact with the siloxanes molecules.

The presence of water limited the adsorption of the D4 into the ACs. In all of the AC samples, around 5% of the D4 that was injected was found in the gas matrix, therefore it was not adsorbed in the AC.

For RB3, the D4 amount extracted is similar both in adsorption and water-partition tests, being higher than 23%. However, the other steam-AC used, Centaur, was able to transform more D4 in the presence of water: Centaur sample showed a drop on the extractable D4 from 32 % in dry conditions to 5% in water-partition tests. H_3PO_4 -AC also showed a higher D4 transformation ratio in the presence of water.

Regarding the composition of the hexane extract of the AC samples, when the water amount available is limited by the humidity of the ACs (adsorption tests) the compounds detected were cyclic siloxanes of higher molecular weight than D4. However, in the water-partition tests, the amount of water required for the D4 hydrolysis reaction is unlimited and the amount of cyclic siloxanes extracted is much lower.

The difference in the distribution of siloxane by-products formed between the adsorption and the water-partition tests, showed the need to do an analysis of the mineral medium, in order to see if the siloxanes were partitioned into more soluble compounds such as the silanediols. Therefore, THF was used as solvent, in order to extract both the polar and the apolar compounds present in the water matrix and retained in the ACs.

The results of Nuchar tests showed the presence of silanediols both in the AC and in the water matrix. Silanediols are formed due to the hydrolysis reaction of D4 catalyzed by the oxygen functional groups of the AC surface. Because of the unlimited water, condensation reactions into cyclic siloxanes do not take place, thus silanediols are found as siloxane transformation products.

The possibility to transform D4 into water soluble silanediols is a result that can help further investigations aiming to remove siloxanes for biogas upgrading technologies. Ongoing research on biological removal of siloxane can use this results and incorporate the AC into biotrickling filters in order to make the siloxanes more bioavailable to the microorganisms. Thus, giving to the biogas utilization a more cost effective technology for the siloxane removal, to help its presence in the market in future years.

7. Acknowledgments

Voldria reconèixer l'esforç i dedicació del pre-doctorat Eric Santos que m'ha ajudat a realitzar els diferents experiments i a entendre els resultats, així com la feina al laboratori. Voldria agrair també la feina de la Dra. Alba Cabrera-codony per el seu ajut de cares a la escriptura d'aquest treball. Agrair a la tutora del Treball de Final de Grau la Dra. Maria Jose Martin Sanchez per haver-me donat la oportunitat de realitzar aquest treball. Finalment agrair el suport del meu Company Yeray Cruz durant el transcurs del treball.

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