

Hybrid Membranes Prepared by the Sol-Gel Process and based on Silica-Polyvinyl Acetate for Methane Enrichment from Biogas

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Abstract

The use of alternative energies to substitute or for using in a less degree the fossil fuels is one of the most important goals of our modern society. Currently research focuses on the production and use of bio-fuels, such as Biogas. However the produced biogas (composed mainly of methane, CH₄) has different undesirable gases such as nitrogen, N₂; carbon dioxide, CO₂ and sulfur compounds, then it is very important to reduce these gases and to increase the concentration of methane gas. Regarding to that our research group is working in some type of hybrid membranes to increase the quality of methane gas in biogas and decrease the concentration of other gases.

The gas separation was accomplished using hybrid membranes prepared by the sol-gel process, based on silica (SiO₂) and polyvinyl acetate, PVAc. The material for the membranes was prepared using different concentrations of SiO₂ (%w/w), and four different solvents (methanol, ethanol, propanol, butanol in different molar ratios) to make compatible the water, necessary for the process, and the tetraethylorthosilicate, TEOS; that is, the precursor of silica. We found that membranes porosity changed depending on the solvent used for the hybrid material preparation. The best membranes were obtained using methanol as solvent. On the other hand, when other solvents were used, the obtained membranes were of bad quality, showing abundant microcracks, visible to the eye, and for this reason they were rejected. For the gas separation tests, pure gases at low pressures similar to that found in bio-digesters conditions were used to test the hybrid membranes. Results showed that diffusion gases order is: H₂, CH₄, N₂ and CO₂. That was corroborated using a mixture of gases, as it is shown.

Keywords: Biogas; Hybrid membranes; Gas separation device

Introduction

Biogas (colorless and flammable gas) is produced from different organic wastes (domestic, agricultural and agro-industrial) [1-4], and it is an alternative kind of energy with high ecological impact. The biogas production is usually made using bio-digesters and the produced gas is composed by approximately 20 - 50% v/v of CO₂, 1- 4% v/v of N₂, small amounts of other gases like Hydrogen, H₂, Hydrogen Sulfide (H₂S) and 50-80% v/v of methane as main component of the biogas [3-5]. Because of this fact, the biogas can be enriched to increase the obtained CH₄ using hybrid membranes [1]. A membrane can be defined as a selective barrier used to separate two different phases and blocks the free transport for one or more components if a mixture is treated. Also it may be defined as a region between two fluids that hinders or favors the movement through it of some gases [6-9]. It is necessary to consider that the size and the shape of the gas molecule affect positively or negatively its movement through the membrane [9]. As it is described, the biogas from biodigesters is a mixture of gases and for this reason to increase the % of methane in it [6] (to enrich the biogas) the use of polymeric membranes has a high potential, due to their low cost investment [7,8].

In the bibliography is mentioned the use of polymeric membranes for the elimination of CO₂ from a gas mixture of H₂, N₂, CH₄, O₂, and CO₂ [10-16] and hybrid membranes (normally an inorganic material with some kind of resins) membranes for a gas separation process [17-26]. Among the means used for gas separation, polymeric membranes have importance due to their advantages such as low cost, high efficiency and low ecological footprint [26,27]. Also some authors discuss how the transport through polymeric membranes follows the solution-diffusion transport mechanism; that is, dissolution of penetrant molecules in the polymer and their diffusion through the membrane [28]. The selection of a suitable polymeric material is crucial in determining the gas separation performance of the membrane. The chemical structure,

crystallinity and morphology of the polymer play an important role in determining the transport properties of the membrane [29]. An article by Thomas Graham was published in 1866, where the author established the basic principles for the diffusion-dissolution model, which governs the transport and gas separation through porous polymeric membranes [30]. On the other hand, the market of gas separation membranes has increased significantly since 1970. In this way some articles and reviews describe the advancement in materials, specifically in polymers, for the production of gas separation membranes [13,28].

In this our current research, we prepared, by the sol-gel process, a hybrid membrane made of polyvinyl acetate and silica for gas separation. This is both a very simple material and easy to prepare and additionally so different from that presented for other researchers. We do not discuss the mechanism for gas separation because this was not the objective of this work. This will be discussed later in other paper. The point is that when we use the material for the preparation of membranes, we have obtained excellent results and it is possible to enrich the methane gas to acceptable levels for being used in motor vehicles or the generation of electricity using motogenerators [1].

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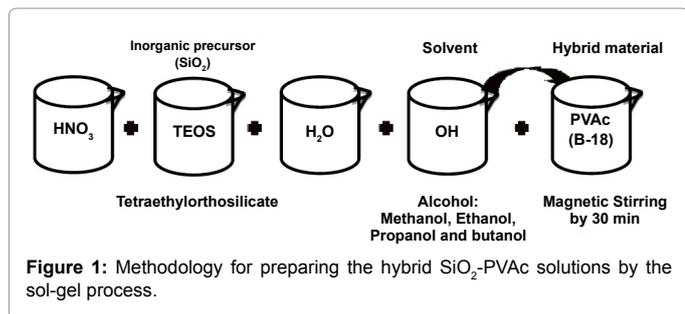


Figure 1: Methodology for preparing the hybrid SiO_2 -PVAc solutions by the sol-gel process.

Methodology for Preparing the Membranes

Hybrid SiO_2 -PVAc (PVAc known commercially as B-18) solutions were prepared by the sol-gel process [31] in concentrations of 30, 35, 40 y 50% w/w of SiO_2 and using four different solvents (methanol, ethanol, propanol and butanol) in different ratios for controlling the porosity. Figure 1 is a schematic representation of the used methodology for preparing the solutions.

Once the hybrid solutions were ready the membranes were made by dip coating, introducing a small piece of stainless steel mesh as a support (275 and 325 mesh) and withdrawing it at a constant rate of 3.33 mm/sec. The membranes prepared as described above were heat treated at 100°C for 30 min. For a second coating the aforementioned steps were repeated, but in this case the time for the heat treatment was only 20 min.

The obtained membranes were characterized by Termogravimetric Analysis (TGA), Optical Microscopy (OM), Scanning Electronic Microscopy (SEM) and Raman Spectroscopy (RS). In addition, CH_4 , H_2 , N_2 and CO_2 pure gases were diffused through the membranes to test their efficiency for the enrichment of methane. Below only the best results using methanol are presented.

Results and Discussion

In Figure 2 it is shown the obtained thermogravimetric analysis, TGA, for the hybrid precursor suspension of 35/65% w/w of silica/PVAc. From the thermogram it is possible to observe that the material loses the larger part of the solvent about 100°C , which it is the limit temperature for annealing the produced membranes. It was determined in some tests, that it is better to anneal the membranes at temperatures no more than 50°C . Higher temperatures to that decrease the adherence of the material to the mesh used as support, giving raise also to the appearing of microcracks and consequently the selectivity of the membrane is low. From the thermogram it is observed also that the used material for the preparation of the membranes is stable about 250°C , beyond that temperature the material suffers degradation. For those reasons it was decided to anneal the membranes at temperatures no longer than 100°C and times of 24 hours for assuring the decreasing of the solvent inside the membrane at acceptable levels and at the same time to obtain the proper porosity.

The inspection of the 35/65 w/w SiO_2 /PVAc membranes under the optical microscopy, using methanol as solvent and annealed at 100°C is presented in Figure 3. Optical microscopy results in Figure 3 shows that membranes are of homogeneous porosity and have small microcracks. When a second coating was deposited over the first one, that microcracks almost disappeared, as it is observed in Figure 3b. When ethanol, propanol and butanol were used as solvents, the obtained membranes were of bad quality, showing abundant microcracks, visible

to the eye, and for this reason they were rejected and not tested for the gas separation process.

These results were corroborated by means of SEM microphotographs in Figure 4. Figures 4a-c shows a good coating when 325 mesh is used. The uniformity of the membrane is attributed to the methanol, which has the smallest size, volatilizes both easily and gradually, properties that help to obtain a proper porosity, with a minimum micro-cracks for the gas separation process.

For determining the ability of the prepared membranes toward the gas separation, some tests were accomplished diffusing pure gases through the membrane and measuring the flow of the exit gases, at an inlet gas pressure of 110 cm in water column. From Figure 5, the diffusion of gases follows the next order: H_2 diffuses first, starting with

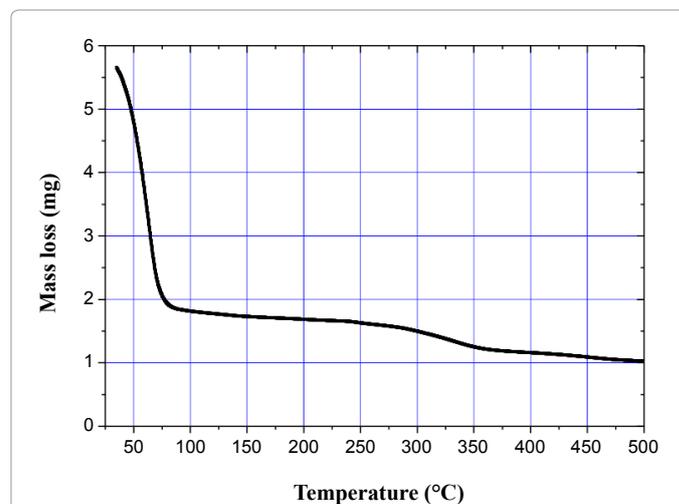


Figure 2: Thermogravimetric analysis, TGA, characterization of the hybrid material with 65 % w/w of PVAc for the preparation of membranes.

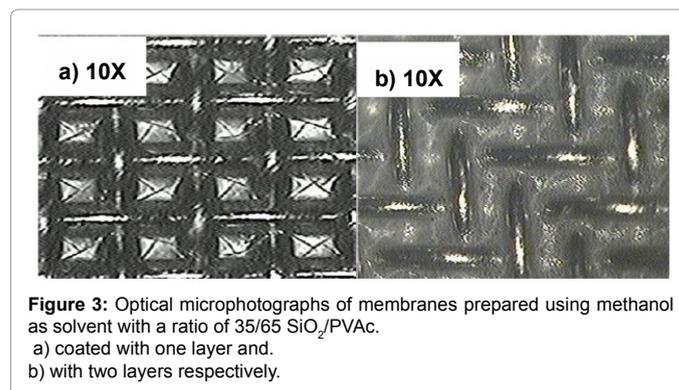


Figure 3: Optical microphotographs of membranes prepared using methanol as solvent with a ratio of 35/65 SiO_2 /PVAc. a) coated with one layer and b) with two layers respectively.

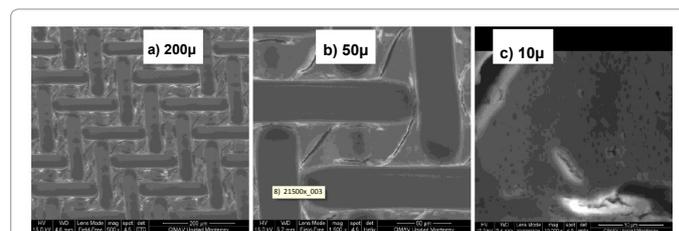
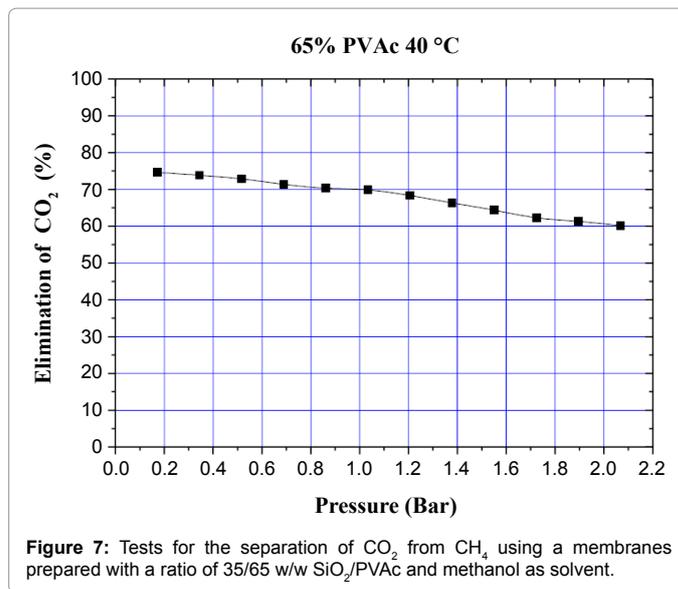
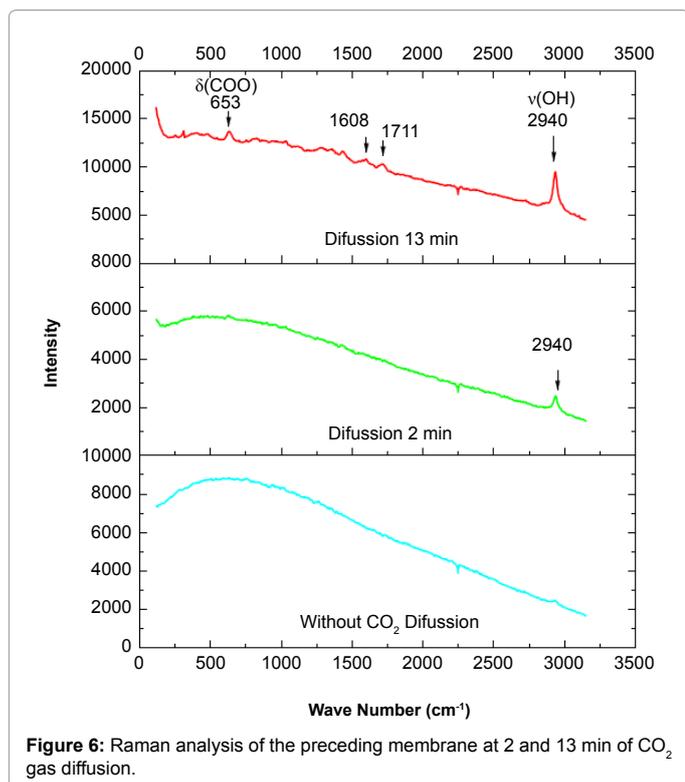
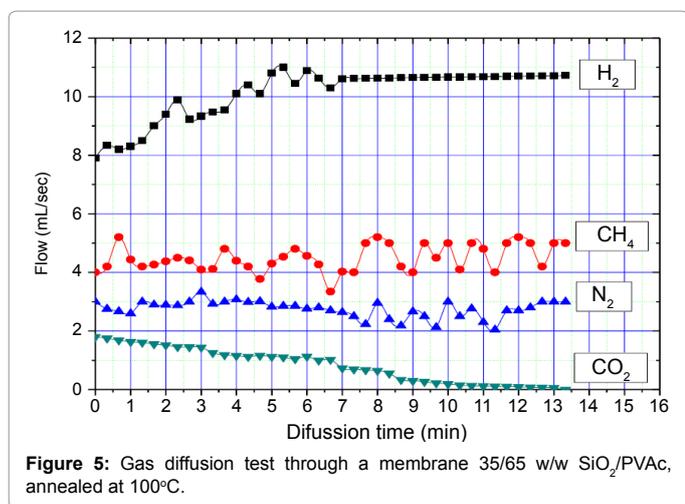


Figure 4: SEM microphotographs of membranes prepared with 35/65 w/w SiO_2 /PVAc, annealed at 100°C and using methanol as solvent in the silica preparation.

a flow of 8 mL/sec, increasing in an approximately exponential way in the next 5 min and after this the flow keeps constant at 10.5 mL/sec. Later CH₄ and N₂ gases were diffused through the membrane with a flow between 4 and 5 mL/sec for methane and between 2 and 3 mL/sec for nitrogen. Finally carbon dioxide diffuses through the membrane, starting with a flow of 2 mL/sec and after 10 min the flow decays to zero.

For establishing why this behavior of the membrane toward the gases, after being prepared the membrane was characterized by Raman Spectroscopy at zero time, after 2 min and then after 13 min of diffusion of CO₂ gas. The results of this characterization are presented in Figure 6. At 2 min, it is clearly demonstrated that during the diffusion of CO₂ some kind of bond between the carbon of the polymer and that of the CO₂ is formed. In this way, the entrapped CO₂ hinders the diffusion of the remaining gases, promoting the selective separation of them.



According to our Raman observations, in the literature has been reported the presence of a very strong band around 2976 cm⁻¹ for the stretching of OH groups and also a band between 641 and 684 wavenumber assigned to δ(COO) groups [32]. Mitterdorfer et al. [33] mention that some di and polycarboxylic acids show the existence of some small Raman bands in the region between 1607 and 1782 cm⁻¹, corresponding to the asymmetric stretching of the C=O group; as a consequence of the connection of the OH group to the carboxylic group or directly to a carbon atom. This can be observed for both the alpha form (1630 cm⁻¹) and the beta form (1608 cm⁻¹). This suggests that the CO₂ was entrapped on the surface and also inside the pores of the membrane or probably it can exist the formation of carbonic acid in those sites. In that way the entrapped CO₂ occupies the existent active sites and consequently hinders the formation of new bonds on the surface of the membrane or inside the pores. The result is an effect of repulsion against the new molecules which try to pass through the membrane. This can explain the selectivity of the membrane to CH₄ gas as it was observed in our experiments (Figure 6).

Additional tests were carried out using the membrane for the separation of methane from a synthetic mixture of methane and carbon dioxide and analyzing the exit gases with an Orsat Analyzer. The tests were run in the same way like that of Figure 5, saturating first the membrane with pure CO₂ gas and then continuing to diffuse a synthetic gas composed of 80.1% of CH₄ and 19.9% of CO₂ under different inlet gauge gas pressures. The results of the elimination of CO₂ are presented in Figure 7. It can be seen from the figure, that 75% v/v of CO₂ was eliminated at 0.17 Bar (2.5 psi) and 60% v/v at 2.07 Bar (30 psi).

From the results it is concluded that it is possible to use these membranes for enriching the methane produced in a biogas. These results are being implemented in a biogas prototype of 10 m³ of materials, putting the membranes in a specially designed device to separate the CO₂ from CH₄.

Conclusions

Supported membranes composed of 35/65 w/w SiO₂/PVAc and annealed at 100°C were prepared to separate with certain selectivity CH₄, CO₂, N₂ and H₂.

Membranes produced using propanol and butanol was of bad quality, with abundant microcracks generated during the drying time, and for that reason were not tested for the gas separation process.

The use of a ratio of 35/65 w/w SiO₂/PVAc and methanol as solvent improves the porosity of membranes. This was enhanced by means of the initial diffusion of CO₂, which is entrapped inside the pores, forming a bond between the carbon of the resin and the carbon of the CO₂.

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