

## Silica/Pebax Monoliths Applied in CO<sub>2</sub> Capture at High Pressure Conditions

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### Abstract

The natural gas (NG) sector represents one of the main sources of the global energy matrix. NG is composed of hydrocarbons, however, it may contain undesirable components, such as nitrogen (N<sub>2</sub>), water (H<sub>2</sub>O), and carbon dioxide (CO<sub>2</sub>). Due to the high H<sub>2</sub>O and CO<sub>2</sub> contents, NG needs to be conditioned on the platforms and the existing processes do not meet the demand. One of the possibilities to increase production and meet the challenges is to design processes at a new pressure level. One of the major challenges is the development of new adsorbents that have CO<sub>2</sub> selectivity, high adsorption capacity and are stable under high-pressure conditions. Therefore, this work aims to synthesize Pebax-1657 silica/polymer monoliths by the sol-gel method and evaluate their structural properties and CO<sub>2</sub> adsorption capacity at different temperatures and up to 50 bar pressure. The physicochemical characterizations proved that the monoliths maintain the structural stability of silica without compromising its textural and thermal qualities. Furthermore, the silica aerogel and silica/Pebax monoliths demonstrated high CO<sub>2</sub> adsorption capacity. These results indicate the effectiveness of the preparation of the monolithic materials and their potential for CO<sub>2</sub> removal under pressurized conditions, making them promising alternatives for application in natural gas purification processes.

*Keywords:* CO<sub>2</sub>; adsorption; high pressure; silica monolith; Pebax.

### 1. Introduction

The Brazilian Pre-Salt fields hold significant reserves of natural gas (NG), characterized by high levels of carbon dioxide (CO<sub>2</sub>), ranging from 30 to 90% in raw NG. Consequently, substantial efforts have been dedicated to finding more efficient adsorbents for gas separation, particularly CO<sub>2</sub>/CH<sub>4</sub> [1]. Among these, monolithic silica aerogel stands out for its exceptional properties: low density, high porosity, low thermal conductivity, and selectivity. Furthermore, its synthesis offers flexibility for modification with amine groups. Generally, the syntheses of these structures are produced in the form of fine powders and therefore are not suitable for direct use in high-scale adsorption processes. To address this issue, an alternative approach is to synthesize the adsorbent in monolith form. Monolith adsorbents offer several advantages over compacted bed adsorbents, such as: reduced pressure drop, leading to more efficient adsorption processes and reduced energy consumption; enhanced mass transfer kinetics, allowing for more

rapid adsorption and desorption processes; manufacturing efficiency, as they can be used immediately after drying, without the need for additional compaction steps [2]. Thus, this study aimed to synthesize monolithic silica aerogel via supercritical drying, characterize its physical and chemical properties, and evaluate its efficacy in CO<sub>2</sub> adsorption under pressurized conditions up to 50 bar, with the goal of developing an advanced adsorbent material for high-pressure CO<sub>2</sub> capture and storage applications.

### 2. Methodology

The silica aerogel monolith (Si-Aeg) was synthesized following the methodology outlined by De Conto [3], undergoing supercritical CO<sub>2</sub> drying at 40 °C and 90 bar for 3 h, while the Pebax-modified aerogel monolith (Si-Peb) underwent a similar process with the addition of a Pebax solution. Physicochemical properties were assessed through FTIR, CHN, and N<sub>2</sub> Adsorption/Desorption analyses.

Measurements of CO<sub>2</sub> (White Martins – 99.5%) adsorption were measured using a high-pressure gas sorption instrument (Isorb-HP1) - Quantachrome. Experimental conditions were chosen to simulate the conditions used in the industry. For the CO<sub>2</sub> the temperatures of 25 °C, 45 °C, 55 °C, and 65 °C were used at a pressure up to 50 bar.

## Results and Discussion

The development of a new Pebax-modified silica aerogel monolith has proven effective, showing a reduction in synthesis time through the sol-gel route combined with supercritical drying. It was observed that the Si-Aeg had a translucent appearance and a fragile structure due to numerous fissures throughout the material (Figure 1, upper). On the other hand, it was noted that the Si-Peb monolith has a more regular formation, greater robustness in monolith shape, and minimized internal cracks (Figure 1, lower).



Fig. 1. Images of Si-Aer and Si-Peb.

The Si-Aer monolith exhibited a specific surface area of 511 m<sup>2</sup>/g and a pore volume of 1.28 cm<sup>3</sup>/g, while the Si-Peb showed values of 277 m<sup>2</sup>/g and 0.58 cm<sup>3</sup>/g, respectively. Through N<sub>2</sub> adsorption/desorption analysis (Figure 2), it was found that Si-Peb has a lower surface area and pore volume compared to Si-Aeg, due to polymer occupying the pores.

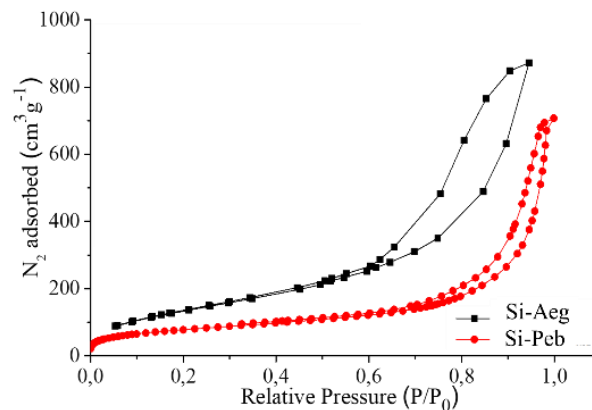


Fig. 2. N<sub>2</sub> adsorption/desorption isotherm for silica aerogel and silica/Pebax monoliths.

The FTIR spectra shown in Figure 3 present the main chemical groups present in the Si-Aeg and Si-Peb monoliths.

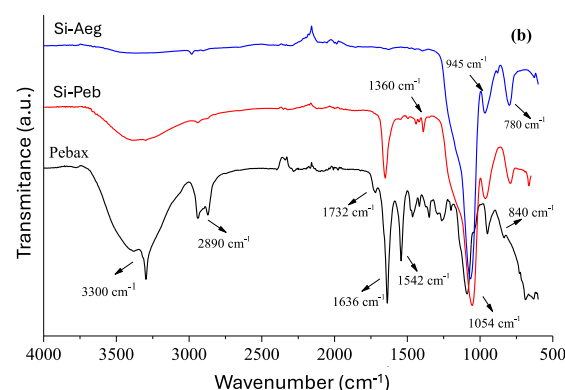


Fig. 3. FTIR spectra of monoliths and Pebax.

The spectrum of pure Pebax was added to observe the contributions of the polymer to the Si-Peb monolith. The functionalization of silica with Pebax silica caused some changes in the position and intensity of the characteristic peaks of Pebax, due to silica-polymer interactions. The peak at 1636 cm<sup>-1</sup> is due to stretching frequency of H-N-C=O group of Pebax, which showed a decline in intensity and a shift to 1641 cm<sup>-1</sup> in the Si-Peb monolith [4]. Pebax peak around 2890 cm<sup>-1</sup>, due to aliphatic -C-H stretching, also reduced its intensity after functionalization of silica aerogel. The broad band at around 3300 cm<sup>-1</sup> on the surface of Si-Peb, is more related to -N-H stretching vibrations of Pebax chain than characteristic of Si-OH groups [4]. The most intense band at 1054 cm<sup>-1</sup> present in Si-Aeg

and Si-Peb corresponds to the asymmetric stretching of Si-O-Si bonds [3, 5]. The peak at  $945\text{ cm}^{-1}$  corresponds to the asymmetric stretching of Si-OH groups, while the symmetric stretching of Si-O-Si chains appears at  $780\text{ cm}^{-1}$  [3, 5].

Adsorption isotherms showed that the  $\text{CO}_2$  adsorption capacity of Si-Peb monoliths decreased with increasing temperature from  $45\text{ }^\circ\text{C}$  to  $65\text{ }^\circ\text{C}$ . The amount of  $\text{CO}_2$  adsorption was  $11.98\text{ mmol g}^{-1}$  at 50 bar and  $45\text{ }^\circ\text{C}$  (Figure 4). The gas adsorption capacity of nanoparticles is greatly affected by gas temperature and pressure, decreasing significantly with increasing temperature [6]. The results also revealed that functionalization with Pebax effectively increased the  $\text{CO}_2$  adsorption capacity, as Si-Aeg at the same conditions reached  $7.34\text{ mmol g}^{-1}$ .

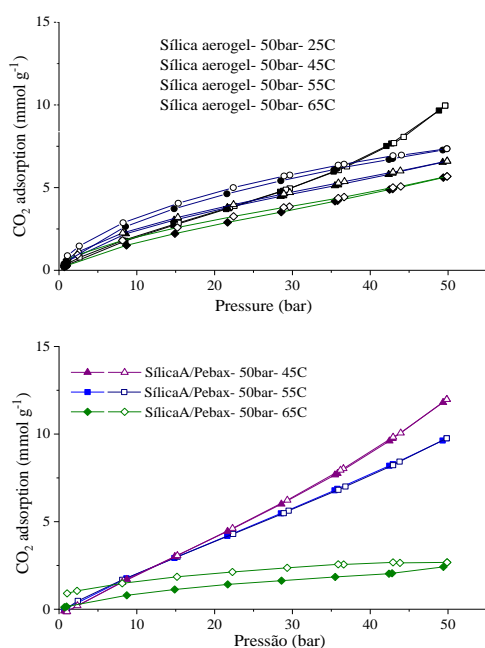


Fig. 4.  $\text{CO}_2$  adsorption isotherms of Si-Aer a) and Si-Peb (b) monoliths under a pressure range between 1 and 50 bar at temperatures of 25, 45, 55 and  $65\text{ }^\circ\text{C}$ .

## Conclusion

The development of a new monolithic material using Pebax in the silica structure has proven effective. It was possible to achieve silica monoliths with a significant reduction in synthesis time through the sol-gel synthesis route combined with supercritical drying. Monolithic silica showed promising results for  $\text{CO}_2$  capture processes with a great adjustment to the Langmuir model. It is noteworthy that this study is new about existing materials, where it is observed that the silica monolith has good  $\text{CO}_2$  adsorption capacity when compared to the literature.

## Acknowledgements

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