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# EXPERIMENTAL EVALUATION OF ACTIVATED CARBON PERFORMANCE FOR CO<sub>2</sub> AND CH<sub>4</sub> ADSORPTION WITH ISOTHERM MODEL ADJUSTMENT

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## Abstract

CO<sub>2</sub> capture and separation technologies are under debate for their importance in mitigating the environmental effects of carbon dioxide emission. An important issue is the separation of CO<sub>2</sub> from pre-salt gas streams, mainly methane. Since Brazilian legislation requires CO<sub>2</sub> concentration in the natural gas stream lower than 3% mol, adsorbent technology is a promising alternative. This work preliminary evaluated the performance of activated carbon to separate CO<sub>2</sub>/CH<sub>4</sub> by using CO<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>/CH<sub>4</sub> equimolar binary mixture adsorption equilibrium isotherm data. The experiments were carried out in a gravimetric sorption analyzer with a magnetic suspension balance at 34°C in a pressure range from 0 to 45 bar. Isotherm models (Langmuir and SIPS) were adjusted to the pure components experimental data as well as Extended Langmuir, IAST Langmuir, and IAST SIPS models predicted the binary mixture behavior. The experimental data fitted the type I isotherm, which is compatible with activated carbon, a microporous structured material, and associated with adsorption in micropores and homogeneous surfaces. The SIPS model provided the best fit for pure component adsorption while IAST Langmuir was the best choice to predict the binary mixture behavior. The results improved understanding of the adsorption process using activated carbon and clarified the adsorption phenomena for CO<sub>2</sub> capture from the pre-salt associate gas scenarios.

*Keywords:* Adsorption; Carbon dioxide; Methane; Activated carbon, Equilibrium isotherm models.

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## 1. Introduction

The climate change and energy transition scenario impose mitigating the effects of CO<sub>2</sub> emission as a major issue. CO<sub>2</sub> capture technologies based on adsorption are promising due to their efficiency in CO<sub>2</sub> capture from a wide range of sources [1]. For example, CO<sub>2</sub> separation from associated pre-salt gas streams is crucial for offshore oil and gas production in Brazil because these streams, mainly composed of CH<sub>4</sub>, have a high concentration of CO<sub>2</sub>, which should be reduced to a maximum of 3% mol for proper commercialization [2]. Due to the limited room for offshore facilities, adsorption has become a recommended separation process in the last few years [3]. The adsorbent selection can improve CO<sub>2</sub> adsorption efficiency as

it considers economic and operational criteria and the ability to separate CO<sub>2</sub> selectively [4]. Such information can be extracted from adsorption equilibrium isotherms, usually built using experimental data collected by gravimetric methods. The top one uses a state-of-the-art analyzer coupled to a magnetic suspension balance for gas sorption/desorption runs. It allows accurate weight measures without the need for further analytical instrumentation and covers large ranges of temperature and pressure [5]. This work evaluated experimentally the activated carbon capacity for CO<sub>2</sub> adsorption from the pre-salt gas streams. Equilibrium isothermal adsorption data were collected using the gravimetric method for (i) pure CO<sub>2</sub>, (ii) pure CH<sub>4</sub> and (iii) the equimolar mixture of CO<sub>2</sub>/CH<sub>4</sub>. Pure component data were used to adjust the parameters of the Langmuir and SIPS models.

The adjusted parameters were then used to predict the adsorption behavior for the binary mixture using Extended Langmuir, IAST Langmuir, and IAST SIPS models. The predicted values were compared with experimental data for the equimolar mixture of CO<sub>2</sub>/CH<sub>4</sub>. The adjusted models also provided a better understanding of the adsorption mechanisms.

## 2. Methodology

The experimental runs were carried out using a gas sorption analyzer coupled to a magnetic suspension balance (MSB), Rubotherm Series IsoSORP SA (150-350, S-SC). The Pressure Swing Adsorption (PSA) method was used to build the equilibrium isotherms of pure CO<sub>2</sub>, pure CH<sub>4</sub>, and a CO<sub>2</sub>/CH<sub>4</sub> equimolar mixture on a commercial pelletized activated carbon sample at 34°C under pressures ranging between 0 and 45 bar. This equipment also allows density to be measured simultaneously with weight for each equilibrium data point.

In sequence, Python® was used to compare model performance through error evaluation. To fit parameters from the adsorption data of pure components and to predict the amount adsorbed for the binary mixture, the equations of Langmuir, Extended Langmuir and Freundlich and Langmuir (SIPS)[6] were used as shown in Eqs. 1, 2 and 3, respectively.

$$q_i = q_{max,i} \frac{K_{e,i} P_i}{1 + K_{e,i} P_i} \quad (1)$$

$$q_i = q_{max,i} \frac{K_{e,i} P_i}{1 + \sum_{j=1}^n K_{e,j} P_j} \quad (2)$$

$$q_i = q_{max,i} \frac{(K_{e,i} P_i)^{a_i}}{1 + (K_{e,i} P_i)^{a_i}} \quad (3)$$

where  $q_i$  (mol/kg) and  $P_i$  (bar) are moles of gas  $i$  adsorbed on the sample and the partial pressure, respectively. The constants  $q_{max}$  (mol/kg),  $K_e$  (bar<sup>-1</sup>) and  $a$  are adjustable parameters related to experimental factors that can interfere with the adsorption rate of gases and their physical meaning can vary depending on each model.

The studied models of Langmuir and SIPS were first applied to describe the equilibrium adsorption isotherm experimental data of each pure gas to adjust their parameters. After that, the estimated parameters were used for predicting the gas mixture

behavior. The partial pressures of CO<sub>2</sub> and CH<sub>4</sub> in the equimolar mixture were used to compute the adsorbed quantities of each gas component, which were summed to predict the total amount adsorbed.

This process was directly used for the Extended Langmuir model while the Ideal Adsorption Solution Theory (IAST) was applied to Langmuir and SIPS models. IAST [6] is a method to calculate the mass of adsorbed gas based on the pressure of the gas mixture, the molar fraction of each component, and the estimated parameters.

Partial pressures were determined from the molar fraction of each component in the gas mixture. Their molar fractions were predicted using the PC-SAFT equation of state [7], and the gas mixture density was measured at equilibrium to obtain the molar fraction of each component after adsorption.

## 3. Results and Discussion

Fig. 1 presents the experimental data collected by gravimetry for the adsorption equilibrium isotherm of the pure gases (CO<sub>2</sub> and CH<sub>4</sub>) and their binary equimolar mixture at 34°C in pressures ranging from 0 to 45 bar.

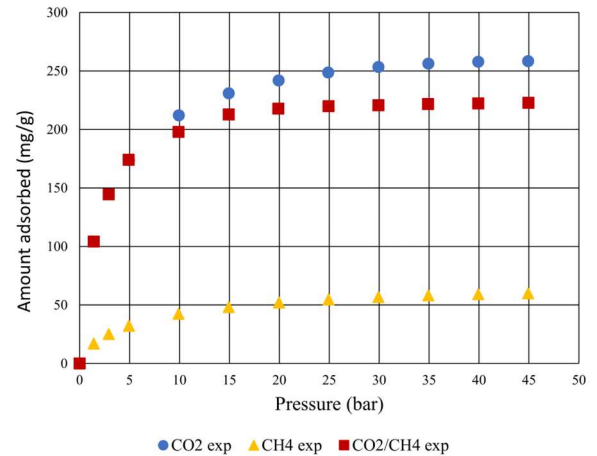


Fig. 1. Adsorption equilibrium isotherms of CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> on activated carbon at 34°C up to 45 bar.

The profile of the isotherms for the pure gases indicates that they follow the Type I behavior according to the International Union of Pure Applied Chemistry (IUPAC) classification [8]. Type I indicates a reversible isotherm and is related to microporous solids with a relatively small external surface in micropores and physisorption on

homogeneous surfaces, which has the amount adsorbed limited by the accessible micropore volume [8]. This is aligned with the type of adsorbent material used since activated carbon has these characteristics. Fig. 1 also shows that the material adsorbs more CO<sub>2</sub> than CH<sub>4</sub>. In NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials [10], there is a lack of data for CO<sub>2</sub> and CH<sub>4</sub> adsorption in activated carbon for 34°C. Moreover, there is no further information on the material type, which makes it difficult to compare the experimental results with the literature. Therefore, this study is significant for reporting new experimental isothermal adsorption data.

Fig. 2 shows the experimental data and the calculated values for CO<sub>2</sub> and CH<sub>4</sub>. The estimated parameters for each model are shown in Tab. 1.

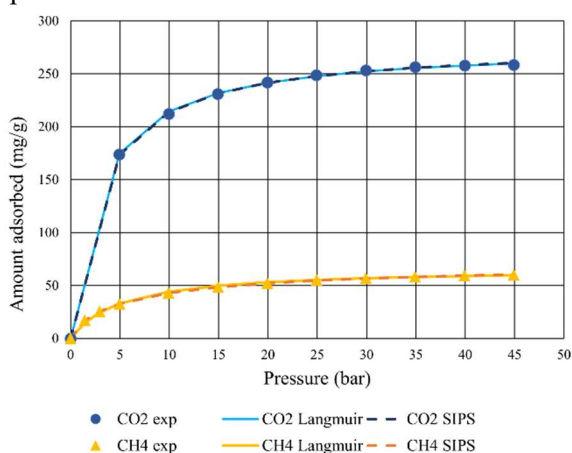


Fig. 2. Adsorption equilibrium isotherms CO<sub>2</sub> and CH<sub>4</sub> on activated carbon at 34°C up to 45 bar.

Tab. 1. Parameters of Langmuir and SIPS and Freundlich models for CO<sub>2</sub> and CH<sub>4</sub> adsorption equilibrium isotherms.

Isotherm	Langmuir		SIPS		
	$K_e$	$q_{max}$	$K_e$	$q_{max}$	$a$
CO <sub>2</sub>	0.347	6.283	0.338	6.307	1.005
CH <sub>4</sub>	0.199	4.139	0.155	4.557	1.245

For the Langmuir model, the fitted parameters were obtained using a least-squares method after model linearization, while for the SIPS model, the parameters were estimated by the minimization function from Python®. The SIPS model reduces to the Langmuir model when  $a$  is 1 [9] and, for the systems evaluated, it was the best one. This was already expected since it has one more parameter ( $a$ ) which accounts for the heterogeneity of adsorption

sites. This can be confirmed by the absolute average deviations: 0.40% and 2.55% for CO<sub>2</sub> and CH<sub>4</sub> for the Langmuir model, respectively, compared to 0.37% and 0.53% for the SIPS model. The  $K_e$  parameter represents the strength of the attraction between adsorbate molecules and the adsorbent surface [6]. Once CO<sub>2</sub> has a higher value for this parameter, it is understood that CO<sub>2</sub> is more attracted to the activated carbon surface, indicating a preference for adsorbing CO<sub>2</sub>.

Langmuir model considers monolayer adsorption, homogeneous distribution of adsorption site, and negligible interaction between adsorbate molecules, which is ideal for representing gas-solid adsorption [9]. SIPS combines Langmuir and Freundlich models and describes homogeneous and heterogeneous systems. It is also stated that SIPS are derived from the Langmuir model and is one of the most applied models for describing monolayer adsorption [9]. For that reason, Langmuir and SIPS have a good fit and these models' assumptions can explain adsorption phenomena. Therefore, Langmuir and SIPS were chosen to predict the CO<sub>2</sub>/CH<sub>4</sub> binary mixture behavior.

Fig. 3 shows the experimental result for CO<sub>2</sub>/CH<sub>4</sub> binary mixture and the predicted values for the Extended Langmuir, IAST Langmuir and IAST SIPS models. Models' deviations are reported in Tab. 3. For the Extended Langmuir model, Eq. 2 was directly applied. For the IAST method, Newton-Raphson was used as a numerical method. The AAD values reported for the binary mixture prediction show that the best model is the IAST Langmuir, a consequence of the model adjusted for the pure components. Even though SIPS had a better fit for the pure component, both models fitted for the pure components had low deviation. So, for the binary mixture, the IAST for Langmuir represented better the data behavior. The low deviations indicate a good prediction and can be used as a parameter analysis before experimenting. The closeness of adsorbed masses obtained from the models and experimental data reveal that the models can represent the adsorption phenomena. This allows a better understanding of the phenomena and evaluation of other adsorbent materials for CO<sub>2</sub> adsorption. The adsorbed amount of each component was obtained using the models for the equimolar CO<sub>2</sub>/CH<sub>4</sub> binary mixture. Higher values of CO<sub>2</sub> captured in the adsorbent than CH<sub>4</sub> were observed leading to the understanding that there is a selectivity towards CO<sub>2</sub> capture.

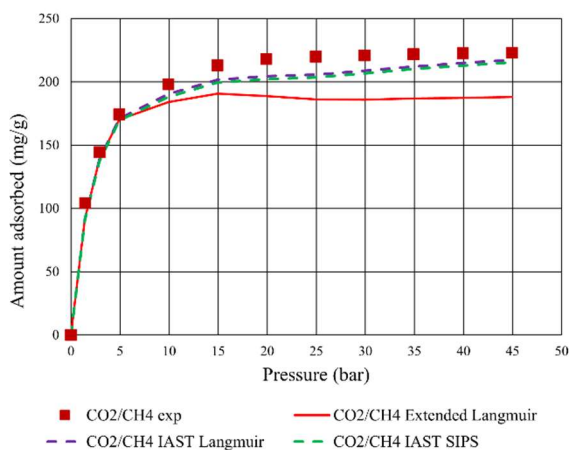


Fig. 3. Adsorption equilibrium isotherms of the equimolar mixture of CO<sub>2</sub>/CH<sub>4</sub> at 34°C up to 45 bar.

Tab. 3. Absolute average deviation (AAD) of model prediction of CO<sub>2</sub>/CH<sub>4</sub> binary mixture adsorption equilibrium isotherm.

	AAD (%)
Extended Langmuir	11.66
IAST Langmuir	5.10
IAST SIPS	6.04

#### 4. Conclusion

Adsorption equilibrium isotherms of CO<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>/CH<sub>4</sub> binary equimolar mixture were determined at 34°C in the pressure range from 0 to 45 bar. The models of Langmuir and SIPS were fitted to the pure component experimental data measured. The parameters estimated for both models were further used by Extended Langmuir, IAST Langmuir, and IAST SIPS models to predict the adsorbed amount of the CO<sub>2</sub>/CH<sub>4</sub> equimolar mixture.

The adsorption equilibrium isotherms revealed a behavior compatible with the porous adsorbent material. The experimental results allied with the models fitting showed a higher amount of CO<sub>2</sub> being adsorbed than CH<sub>4</sub>, which could qualitatively indicate a selectivity towards CO<sub>2</sub>. Since SIPS model had a better fit, it is possible to consider that its premises describe well the adsorption mechanism for this type of activated carbon. The IAST Langmuir model provided the lowest AAD value for

the mixture behavior prediction indicating an adsorbent preference for CO<sub>2</sub>.

Finally, this study used a high-accuracy gravimetric analyzer for gas adsorption, showing how useful this technique is for building isotherms. Due to the lack of CO<sub>2</sub> and CH<sub>4</sub> adsorption data at 34°C, these new experimental data are a valuable contribution. The results offer insights about CO<sub>2</sub> capture, reinforcing the need for more data to better understand materials capacity and applicability towards a cyclic adsorption process development.

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