Adsorption performance indicators for the CO₂/CH₄ separation: application to biomass-based activated carbons

N. Álvarez-Gutiérrez, M. V. Gil, F. Rubiera, C. Pevida*

Instituto Nacional del Carbón, INCAR-CSIC. Apartado 73, 33080 Oviedo, Spain.

*corresponding author e-mail: cpevida@incar.csic.es

Abstract

A deep understanding of the interaction and competition between different gases on adsorption processes is essential for the design and optimization of industrial units. Two biomass-derived activated carbons (CS-CO₂ and CS-H₂O), synthesized in our laboratory, were evaluated as selective adsorbents for the separation of CO₂ from CO₂/CH₄ mixtures. Adsorption isotherms of the pure gases (i.e., CO₂ and CH₄) were performed in a high-pressure magnetic suspension balance at three different temperatures (303, 323 and 343 K) up to 1000 kPa and the data were correlated using the Sips and Toth models. The Ideal Adsorbed Solution Theory (IAST) was applied to predict the binary adsorption equilibrium. The results were validated by means of experimental breakthrough tests in a fixed-bed set-up. The isosteric heats of adsorption were estimated from the pure component adsorption data by means of the Clausius-Clapeyron equation and the Sips and Toth equations. All of the equilibrium data were integrated in a performance indicator defined so as to be able to evaluate the adsorbent in terms of selectivity, working capacity and adsorption enthalpy under conditions relevant to the specific application. Although both CS activated carbons had similar textural features, CS-CO₂ showed a better overall performance than CS-H₂O for the

separation of CO₂ from CO₂/CH₄ mixtures. Our results highlight the importance of carrying out a deep analysis of the adsorption equilibrium under conditions relevant to the foreseen application in order to identify the most suitable adsorbent.

Keywords: Adsorption; CO₂/CH₄ separation, adsorption performance indicator; biomass

1. INTRODUCTION

Carbon dioxide and methane are the main gases responsible for global warming; the impact of methane in terms of global warming potential is greater than that of carbon dioxide, although CO₂ emissions are quantitatively more important. Both gases are commonly found in gas mixtures such as natural gas, landfill gas, coalbed methane and biogas [1]. Upgrading biogas is commonly utilized. With minor cleanup, biogas can be used to generate electricity and heat. When processed to a higher purity standard, biogas is called renewable natural gas and can be used as an alternative fuel for natural gas vehicles or to produce hydrogen via steam reforming for fuel cells. Another alternative for the valorization of biogas is the production of syngas to be used as the basis for manufacturing valuable chemicals [2]. It is generally accepted that the utilization of biogas will help to minimize the amount of CH₄ released to the atmosphere. However prior to use, the carbon dioxide content of the biogas must be reduced in order to increase the heating value of the methane and to avoid pipeline and equipment corrosion in the presence of water [3-5]. The separation of carbon dioxide to upgrade methane is of critical economic importance and is still a subject of intensive research [6, 7]. Different technologies are available for this purpose, such as absorption processes

[8], membrane separation [9-11], cryogenic distillation [12-14] and adsorption [15-17]. Adsorption-based processes that employ microporous materials constitute a very promising cost-efficient technology. In a Pressure Swing Adsorption (PSA) process the adsorbent is regenerated by lowering the pressure, whereas in a Temperature Swing Adsorption (TSA) operation the regeneration is carried out by increasing the temperature [18]. Due to its simple control, low operating and capital investment costs and higher energy efficiency, PSA is commonly considered to be the most attractive and efficient process for biogas upgrading [15, 19-22].

A variety of microporous materials, such as activated carbon (AC), zeolites, and metal-organic frameworks (MOFs) have been considered for carrying out CO₂ separation [23-28]. The use of activated carbons has been widely investigated [29-36] due to their large surface area, high micropore volume, suitable pore size distribution and hydrophobic character [37].

One of the main challenges in the commercial manufacture of activated carbons is to identify new precursors that are cheap, accessible and available in abundant quantities. Agricultural by-products, such as fruit stones, are for these reasons particularly appealing and they may be a source of substantial economic rewards. In Spain, large amounts of cherry stones are generated as wastes in the industrial production of Kirsh (cherry brandy) and jam, especially in the region of Extremadura (production of cherry > 36 t per year) and in the region of Aragón (production of cherry > 25 t per year) [38]. Previous studies have shown that cherry stones are attractive as precursors of high porosity carbons with yields similar to those reported for other fruit stones [39-42]. Adsorption on cherry stone-based activated carbons in the liquid phase has found application in the food industry

[43], in the water and wastewater treatment [44-46], in the chemical and pharmaceutical industry [47] and in the textile industry [48]. Moreover, cherry stones have been tested for specific applications such as electrode materials [49-51]. However, to the best of our knowledge, there are no reports on the application of cherry stone-based activated carbons to the separation of CO₂/CH₄.

Extensive work is being undertaken on the adsorption equilibrium of pure gases (e.g. CH₄ and CO₂) on different adsorbents at pressures below 1000 kPa mainly because it is relatively easy to evaluate in commercial laboratory appliances [52-55]. However, experimental measurement by means of multi-component adsorption isotherms over wide ranges of pressure, temperature and feed gas compositions, which is necessary to predict the competitive adsorption behavior of gas mixtures, is time-consuming and sometimes difficult to carry out experimentally with sufficient accuracy. To this end, empirical models have been developed to predict multi-component adsorption on the basis of single-component adsorption data [56, 57]. Nevertheless, validation of the model with experimental multi-component adsorption data is required, particularly in the case of high pressure adsorption [58].

Herein we present a systematic study of the main parameters involved in the equilibrium of CO₂ and CH₄ adsorption, which is the basis of most adsorption processes. We have gravimetrically measured pure component adsorption isotherms of CO₂ and CH₄, on two cherry stone-based activated carbons previously prepared in our laboratory: a pressure range of up to 1000 kPa and three different temperatures (303, 323 and 343 K) have been evaluated. The Ideal Adsorbed Solution Theory (IAST) has been applied to predict the binary adsorption

of CO₂/CH₄ on the basis of single component gas adsorption fittings to the Sips and Toth models. In addition, the heat of adsorption and the selectivity of the cherry stone-based activated carbons for separating CO₂ from a biogas representative CO₂/CH₄ mixture have been calculated. All these parameters have been integrated in a performance indicator so as to establish the potential of the produced biomass-based activated carbons for biogas upgrading under real conditions.

2. MATERIALS AND METHODS

2.1 MATERIALS

Two activated carbons, CS-CO₂ and CS-H₂O, previously obtained in our laboratory from a low-cost biomass precursor, cherry stones, were evaluated as adsorbent materials. CS-CO₂ was prepared in a single-step activation using carbon dioxide, whilst CS-H₂O was prepared using steam as activating agent. Details on the preparation protocol as well as the chemical and textural characterization can be found elsewhere [59].

Table 1 summarizes the main characteristics of the evaluated adsorbents. CS-CO₂ and CS-H₂O present apparent BET surface areas of 1045 and 998 m² g⁻¹, respectively, and well-developed microporosity (N₂ micropore volume of 0.40 and 0.38 cm³ g⁻¹, respectively). Narrow micropore volumes account for the majority of the microporosity (73-62%) in the produced carbons.

Table 1. Characteristics of the CS-based activated carbons

	CS-CO ₂	CS-H ₂ O
<u>N₂ adsorption at 77 K</u>		
BET surface area (m ² g ⁻¹)	1045	998
Total pore volume (cm ³ g ⁻¹)	0.48	0.53
Micropore volume (cm ³ g ⁻¹) ^a	0.40	0.38
Average micropore width (nm) ^b	0.93	0.89
<u>CO₂ adsorption at 273 K</u>		
Narrow Micropore volume (cm ³ g ⁻¹) ^a	0.35	0.33
Average narrow micropore width (nm) ^b	0.78	0.74
<u>Bed characteristics</u>		
Mass of adsorbent (g)	4.08	4.80
Particle size (mm)	1-3	1-3
Total porosity, ϵ_T	0.86	0.84
Helium density (g cm ⁻³) ^c	1.98	1.99
Apparent density (g cm ⁻³) ^d	0.53	0.64
Bed diameter (cm)	1.30	1.30
Bed height (cm)	11.55	11.65
Bed density (g cm ⁻³)	0.27	0.31

^a Evaluated with the Dubinin-Radushkevich equation.

^b Assessed from the Stoeckli-Ballerini relation.

^c Determined by He pycnometry.

^d Determined with Hg porosimetry.

CO₂ and CH₄ were evaluated as adsorptive gases and were both supplied by Air Products with purities higher than 99.995%. Helium was used as a non-adsorptive gas in the gravimetric measurements to correct the buoyancy effect and also as a purge gas in the breakthrough experiments.

2.2 EXPERIMENTAL DEVICES

2.2.1 Pure Gas Component Adsorption Isotherms

Adsorption isotherms of the CO₂ and CH₄ were performed in a high-pressure Rubotherm-VTI magnetic suspension balance. This instrument compensates for most of the drawbacks of the gravimetric technique by physically separating the sample from the high resolution balance by means of magnetic

suspension coupling [60]. Three different temperatures (303, 323 and 343 K) in a pressure range from 0 to 1000 kPa were selected for the evaluation. Prior to adsorption, the sample was dried in situ under vacuum at 373 K for 120 min. Experiments with helium were carried out in order to determine the volume of the adsorbent and cell system, enabling the effect of buoyancy on the measurements to be evaluated. The absolute amounts of CO₂ and CH₄ adsorbed over the pressure range tested were estimated following the procedure described in previous works [58, 61].

2.2.2 Binary Gas Mixture Adsorption Measurements: Breakthrough Experiments

Binary breakthrough adsorption experiments of CO₂/CH₄ were conducted in a fixed-bed set-up packed with the biomass activated carbons (approximately 4 g). The stainless steel fixed-bed column is 13.3 cm in height, 1.3 cm in diameter (i.d.) and is equipped with a porous plate located 4.7 cm from the base of the column. More details about the set-up can be found elsewhere [62]. A mass flow meter, M13 mini CORI-FLOW meter from Bronkhorst, was incorporated to the set-up to measure the flow rate of the effluent through the adsorbent bed.

A simulated biogas, CO₂/CH₄ mixture (50/50 vol. %), was fed (30 mL/min STP) to the adsorption unit and the adsorption performance of the samples was evaluated at 300 kPa and at 303 K. The amounts of CO₂ and CH₄ adsorbed at equilibrium under different temperatures and CO₂ and CH₄ partial pressures can be determined by applying a mass balance equation to the bed but taking into consideration the gas accumulated in the intraparticle voids and dead spaces of the bed. More details about the calculation procedure can be found in *Gil et al.* [63].

2.3 THEORETICAL

2.3.1 Single component adsorption

Adsorption models are very useful as they can predict the behavior of the equilibrium of adsorption over a wide temperature and pressure range. Two empirical models were selected to fit the single component adsorption data (absolute loadings) of CO₂ and CH₄ on the cherry stone-based activated carbons: the Sips and Toth models. These two models are widely used, as they applied to a wide range of pressure and temperature sorption data.

The general form of the Sips model is represented in Eq. (1):

$$q = q_s \frac{(bP)^{1/n}}{1+(bP)^{1/n}} \quad (1)$$

In this equation, q represents the concentration of the adsorbed species, P is the equilibrium pressure and q_s , b and n are the maximum adsorption capacity, the adsorption equilibrium constant and the parameter indicating the heterogeneity of the system, respectively. This heterogeneity (n), which may have originated from the solid structure, the solid energy properties or the adsorbate, is usually greater than unity. Therefore the larger it is, the more heterogeneous the system is. When n is unity, the model assumes the appearance of the Langmuir equation. As a first approximation, q_s was considered to be temperature independent and b , and n were considered to be temperature dependent [56]:

$$b = b_0 \exp \left[\frac{Q}{RT_0} \left(\frac{T_0}{T} - 1 \right) \right] \quad (2)$$

$$\frac{1}{n} = \frac{1}{n_0} + \alpha \left(1 - \frac{T_0}{T} \right) \quad (3)$$

In the above equations, b_0 , n_0 , α are the constants associated to the temperature dependent equations; R is the universal gas constant and T is the temperature. Q is the isosteric heat at a fractional loading of 0.5 and T_0 is the reference temperature which, in this case, is 303 K.

The Sips model may not be accurate in the low pressure range as it does not follow the Henry law pattern of behavior. An alternative model for fitting the pure component data that satisfies both the low and high pressure ranges is the Toth model, which has the following form:

$$q^* = q_s^* \frac{b^* P}{[1 + (b^* P)^t]^{1/t}} \quad (4)$$

where q^* represents the concentration of adsorbed species, q_s^* the saturation capacity and P the pressure of the adsorptive. The parameters b^* and t are specific for adsorbate-adsorbent pairs. When $t=1$, the Toth isotherm is simplified to the Langmuir equation. Hence, like n in the Sips equation, the parameter t is said to characterize the system's heterogeneity. However, t is usually less than unity.

As in the Sips equation described so far, the temperature dependence of the equilibrium parameters in the Toth equation also needs to be considered [56]:

$$t = t_0 + \alpha^* \left(1 - \frac{T}{T_0}\right) \quad (5)$$

In the above equation, t_0 and α^* are the constants associated to the temperature dependence of t . The b^* dependence with temperature is similar to the b dependence in the Sips model but in this model, Q is a measure of the isosteric heat of adsorption at zero fractional loading.

The temperature dependence of each parameter in the Sips and Toth models was determined by simultaneous fitting of the adsorption isotherms at the

three temperatures studied. For this purpose the Excel tool Solver (Microsoft Office Excel 2007) was used departing from values of q_{s,CO_2} and q_{s,CO_2}^* of 2, q_{s,CH_4} and q_{s,CH_4}^* of 1, n_0 and t_0 of 1, α of 1 and b_0 and b_0^* of 0. The goodness of the fit was evaluated on the basis of the minimum residual sum of squares (SSR) at the three evaluated temperatures, as follows:

$$SSR(\%) = \sum_{T_1}^{T_3} \left(\frac{\sum_{j=1}^N (q_{exp,i} - q_{mod,i})^2}{N} \right) \times 100 \quad (6)$$

where $q_{exp,i}$ and $q_{mod,i}$ are the experimental and predicted amounts adsorbed, respectively, T_1 to T_3 are the three tested temperatures, j is the number of points per isotherm and gas component, i represents the component in the binary mixture (CO_2 and CH_4) and N is the total number of experimental data points. Hence, the goodness of the fit of each model is assessed from the minimum SSR value.

2.3.2 Multicomponent adsorption

Using the fitted parameters from the pure component experimental adsorption data, predicted adsorption data for a binary mixture of CO_2 and CH_4 were generated by means of the Ideal Adsorbed Solution Theory (IAST) of Prausnitz and Myers [64, 65]. Based on thermodynamics, IAST is a predictive model which does not require any gas mixture data and is independent of the actual model of physical adsorption. IAST is analogous to Raoult's law for the vapor-liquid equilibrium, which assumes an ideal behavior to represent the relationship between the bulk gas phase and adsorbed phase. The Matlab IAST code constructed by Do [56] was used to predict multicomponent CO_2/CH_4 adsorption using the pure component Sips and Toth model fittings.

2.3.3 Isosteric heat of adsorption

The isosteric heat of adsorption of the components of a gas mixture is an important parameter for the proper design and operation of any gas-phase adsorption process. It is defined as a partial derivative of the change in the enthalpy of the system with respect to the amount adsorbed at a certain temperature, pressure, amount adsorbed and surface area [66]. This parameter reveals the degree of energetic heterogeneity of the gas-solid interactions. An increase in heat of adsorption with gas loading is characteristic of homogeneous adsorbents with constant gas-solid energies of interaction. This increase is due to cooperative interactions between the molecules adsorbed. On the other hand, a decrease in the heat of adsorption with gas loading is ascribed to highly heterogeneous adsorbents with a wide distribution of gas-solid energies of interaction. Finally, a constant heat of adsorption with gas loading indicates a balance between the strength of cooperative gas-gas interactions and the degree of heterogeneity of gas-solid interactions [67].

For any given isotherm model, the isosteric heat of adsorption, Q_{st} , is typically estimated using the Clausius-Clapeyron equation as follows:

$$\frac{Q_{st}}{RT^2} = \left(\frac{\partial \ln P}{\partial T} \right)_{n^*} = \ln \frac{P}{P_0} = -\frac{Q_{st}}{RT} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (7)$$

where n^* is the specific amount adsorbed at a pressure P and temperature T . A plot of $\ln P$ against $1/T$ gives a straight line whose slope represents Q_{st}/R .

The heat of adsorption determines the temperature changes inside the adsorber during the ad/desorption steps of the process, which, in turn, govern the local adsorption equilibria and kinetics, and, consequently the overall performance

of the process [68]. The Clausius-Clapeyron equation has been applied to estimate the heat of adsorption of CO₂ and CH₄ on CS-CO₂ and CS-H₂O.

3. RESULTS AND DISCUSSION

3.1 PURE COMPONENT CO₂ AND CH₄ ADSORPTION ON ACTIVATED CARBON

The single-gas adsorption isotherms of CO₂ and CH₄ measured at 303, 323 and 343 K up to 1000 kPa on samples CS-CO₂ and CS-H₂O are shown in Figure 1. The solid lines correspond to the Sips model, the dashed lines correspond to the Toth model and the solid points represent the experimental data for CS-CO₂ (circles) and CS-H₂O (squares).

Figure 1. Adsorption equilibrium isotherms of CO₂ (a), and CH₄ (b) on CS-CO₂ (circle symbols) and on CS-H₂O (square symbols) at 303, 323 and 343 K. Solid points represent experimental data. The solid lines show the fitting to the Sips model and the dashed lines the fitting to the Toth model.

For both CO₂ and CH₄ the equilibrium adsorbed amounts increase, as the pressure in the system increases although the slope decreases at higher pressures since the adsorption sites are then approaching saturation. The adsorption isotherms also show that at under similar process conditions of pressure and temperature, the amount of CO₂ adsorbed is significantly greater than the quantity of CH₄ adsorbed. This phenomenon can be ascribed to the large quadrupole moment of CO₂ compared to CH₄ (CH₄ does not have a quadrupole moment). This property leads to a higher affinity of the adsorbent surface for CO₂ which results in an increased uptake. As can be seen in Figure 1 temperature strongly affects the equilibrium adsorption capacity at a given pressure. In an adsorptive separation process, the temperature is increased during the adsorption step due to the exothermic nature of the adsorption process, whereas it is diminished during desorption, which is an endothermic process. This thermal effect tends to undermine the performance of the adsorbent, as it reduces the equilibrium capacity during the adsorption step whereas it increases it during the regeneration step. If the performance of both samples towards CO₂ and CH₄ adsorption is compared, striking similarities can be observed: CS-CO₂ only attains slightly greater uptakes in the higher pressure range that may be in agreement with the small differences in the volume of micropores (0.40 cm³ g⁻¹ for CS-CO₂ and 0.38 cm³ g⁻¹ for CS-H₂O).

The goodness of the fittings between the experimental values and the Sips and Toth models at the three different temperatures for CO₂ and CH₄ adsorption on CS-CO₂ and CS-H₂O have been plotted (lines) in Figure 1. The estimated fitting parameters and the sum of the squared residuals (SSR) are tabulated in Table 2.

As can be seen from Figure 1, the excellent agreement between the fittings of both models and the experimental data demonstrates that these isotherm models can be employed to accurately correlate the adsorption equilibria of the two adsorbates. This goodness of fitting is corroborated by the small values of the SSR reported in Table 2. The amounts adsorbed at saturation conditions, as predicted by the models for both samples, are always greater for CO₂ than for CH₄. This implies selectivity of the adsorbents towards CO₂.

Table 2. Fitting parameters of the Toth and Sips models to the single component CO₂ and CH₄ adsorption isotherms for CS-CO₂ and CS-H₂O

Sample	Model	Component	<i>T</i> (K)	<i>q_s</i> and <i>q_s[*]</i> (mol/kg)	<i>b</i> and <i>b[*]</i> (kPa ⁻¹)	<i>n</i> (Sips) <i>t</i> (Toth)	<i>Q</i> (kJ/mol)	<i>α</i> and <i>α[*]</i>	SSR (%)
CS-CO ₂	Sips	CO ₂	303	10.88	0.0017	1.38	19.12	0.37	0.30
			323		0.0010	1.34			
			343		0.0007	1.30			
		CH ₄	303	6.25	0.0014	1.26	16.32	0.43	0.07
			323		0.0010	1.21			
			343		0.0007	1.18			
	Toth	CO ₂	303	18.07	0.0059	0.39	29.60	0.47	0.22
			323		0.0028	0.42			
			343		0.0015	0.45			
		CH ₄	303	8.90	0.0029	0.51	23.12	0.52	0.06
			323		0.0016	0.54			
			343		0.0010	0.57			
CS-H ₂ O	Sips	CO ₂	303	9.90	0.0018	1.40	23.04	0.02	0.25
			323		0.0010				
			343		0.0006				
		CH ₄	303	5.96	0.0014	1.24	18.71	0.00	0.05
			323		0.0009				
			343		0.0006				
	Toth	CO ₂	303	14.45	0.0065	0.43	23.33	0.02	0.18
			323		0.0037				
			343		0.0022				
		CH ₄	303	8.36	0.0026	0.53	18.30	0.00	0.03
			323		0.0017				
			343		0.0011				

It is worth noting that the amounts adsorbed at saturation estimated by the Toth model (q_s^*) are greater than those predicted by the Sips model (q_s). This discrepancy is probably due to the fact that the experimental adsorption data only spanned fractional loadings (q/q_s or q^*/q_s^*) of up to about 0.5 [69]. The use of the Sips equation generally results in higher fractional loadings for any given pressure.

The parameters n (Sips model) and t (Toth model) reflect the heterogeneity of the system. Comparison of these values in Table 2 reveals that the deviation of n and t from unity is more noticeable for CO₂ than for CH₄. This suggests more specific interactions of CO₂ on CS-CO₂ and CS-H₂O. In the same way, the estimated values for the CS-CO₂ and CS-H₂O systems suggest similar heterogeneity in both systems.

The affinity parameter, b , decreases with the increase in adsorption temperature. This could be ascribed to the higher coverage and stronger affinity of the adsorbate towards the adsorbent surface at lower temperatures.

3.2 PREDICTION OF BINARY ADSORPTION EQUILIBRIA FROM SINGLE COMPONENT DATA

Figure 2 shows the uptake *versus* total pressure of multicomponent gas adsorption equilibria, as predicted from the IAST-Sips and IAST-Toth (solid and dashed lines, respectively) models for a binary gas mixture of CO₂ and CH₄ (50/50 vol.%).

Figure 2. n^+-P diagrams for the CO_2/CH_4 (50/50 vol.%) adsorption at 303.15 K on CS- CO_2 (a) and CS- H_2O (b). Experimental points at 300 kPa (squares), Sips fitting pure (circles), Toth fitting pure (triangles), binary IAST-Sips (solid lines) and binary IAST-Toth (dashed lines). The red color corresponds to CO_2 and the blue to CH_4 . Please refer to the electronic version for color assignments.

The single-gas fitting parameters in Table 2 were used for these predictions. To evaluate the reliability of the prediction, breakthrough experiments with a feed gas of the same composition were carried out at 300 kPa and at 303 K (square symbols in Figure 2). The predicted CO₂ and CH₄ loadings under these conditions are compared to the experimental values estimated from the dynamic experiments in Table 3. The relative error (*RE*) is estimated as follows:

$$RE(\%) = \left| \frac{q_{meas} - q_{calc}}{q_{meas}} \right| \times 100 \quad (8)$$

where, q_{meas} is the experimental uptake from the breakthrough experiments and q_{calc} is the value predicted by IAST.

Table 3. Comparison between the adsorbed amounts of CO₂ and CH₄ from dynamic experiments and those obtained from the IAST model prediction at 303 K and 300 kPa

	Experimental uptake (mol/kg)		IAST- Sips model (mol/kg)				IAST-Toth model (mol/kg)			
	CO ₂	CH ₄	CO ₂	RE (%)	CH ₄	RE (%)	CO ₂	RE (%)	CH ₄	RE (%)
CS-CO ₂	2.69	0.62	2.60	3.3	0.68	9.7	2.50	7.1	0.72	16.1
CS-H ₂ O	2.41	0.72	2.48	2.9	0.62	13.8	2.51	4.1	0.64	11.1

According to the values in Table 3 IAST adequately estimates the CO₂ uptakes on samples CS-CO₂ and CS-H₂O. Greater deviations between the experimental and predicted values are observed in the CH₄ uptakes. Regarding the two CS samples, the IAST-Sips prediction seems to be more precise for CS-CO₂, in terms of the loading of CO₂ (maximum deviations of up to ±3.3%) and CH₄ (maximum deviations of ±9.7%). In the case of CS-H₂O both models seem to

predict binary adsorption with a similar degree of accuracy. Globally, IAST models predict the experimental performance at 300 kPa with a good degree of accuracy for both samples.

Valenzuela and Myers [70] who tested the combination of the IAST with the Toth and Sips equations stated that the IAST predictions are independent of the particular equation adopted for the pure gas isotherms. The requirement is a high fit quality between the single gas experimental data and those calculated with the selected model.

Figure 2 also displays the pure component adsorption prediction as estimated by the Sips (circular symbols) and the Toth model (triangular symbols) for reference purposes. The binary adsorption isotherms of the mixture of CO₂ and CH₄ are well below those of the pure components. The adsorptive performance is greatly influenced by the gas mixture firstly due to the reduction in the partial pressures of the components when mixed. The extent to which CO₂ and CH₄ adsorption is reduced from the single to the binary adsorption system is different: the presence of CO₂ (strongly adsorptive) drastically reduces the adsorption of CH₄ (weakly adsorptive) in the equimolar CO₂/CH₄ binary mixture. In this sense, CO₂ adsorption from the binary mixture at 300 kPa accounts for more than 85% of the adsorption capacity of the pure component at a similar partial pressure (150 kPa) whereas CH₄ only accounts for about 50%.

3.3 ISOSTERIC HEATS OF ADSORPTION

As well as isotherm data, isosteric heats of adsorption are required since they influence the equilibrium of adsorption and are crucial to the energy and mass

balances of the adsorption process. The isosteric heat of adsorption as a function of the loading or amount adsorbed was estimated by applying the Clausius-Clapeyron equation (Eq. 7) to the single component adsorption data obtained with the high-pressure magnetic suspension balance. The results are shown in Figures 3a and 3b. The values predicted by the Sips and Toth models are also plotted in Figure 3. The analytical equations used for these calculations can be found elsewhere [56].

Figure 3. Isosteric heats of adsorption of CO₂ (a) and CH₄ (b) on CS-CO₂ (blue triangles) and CS-H₂O (red circles) as estimated by the Clausius-Clapeyron equation. The solid lines represent the value from the Sips model and the dashed lines from the Toth model. Please refer to the electronic version for color assignments.

According to the Sips and Toth models the isosteric heat of adsorption is independent of the loading for CS-H₂O whereas it is dependent for CS-CO₂. In this sense, even though the Sips model resulted in higher fractional loadings than the Toth model, the values estimated for the heats of CO₂ and CH₄ adsorption on CS-H₂O by both models are nearly coincident and in good agreement with the average isosteric heat of adsorption estimated from the experimental pure gas adsorption data. On the other hand, for CS-CO₂ the dependency on the loading accounts for the differences between the estimation of both models: values obtained using the Sips equation are approximately +2 kJ/ mol (CO₂) and +1 kJ/ mol (CH₄) than those from the Toth model. This is consistent with the aforementioned higher fractional

coverage obtained for any given pressure by means of the Sips equation. On the other hand, Sips estimation shows good correspondence to the experimentally-derived data, particularly in the higher CO₂ and CH₄ loading range. Toth estimation for CS-CO₂ significantly deviates from the heats of CO₂ and CH₄ estimated from the Clausius-Clapeyron equation.

In Figure 3a the isosteric heat of adsorption of CO₂ for CS-CO₂, as estimated from the experimental pure component data, displays a decreasing trend with increasing loading which suggests energetic heterogeneity. For CS-H₂O the isosteric heat of CO₂ adsorption shows an initial decreasing trend at low coverage (< 1.2 mol/kg) but then remains practically constant with loading (≈23 kJ/mol). However, the heat of adsorption of CO₂ for CS-H₂O is shifted approximately + 2 kJ/mol above that of CS-CO₂. Likewise, the isosteric heat of adsorption for CH₄ follows different trends for the two adsorbents, as can be observed in Figure 3b. In the case of CS-CO₂ it increases with the amount of gas adsorbed up to about 1.4 mol/kg and then decreases. This maximum suggests that there exist no specific adsorption sites for the adsorption of CH₄ in CS-CO₂. The isosteric heat of adsorption of CH₄ on CS-H₂O remains practically constant (≈18 kJ/mol) in the evaluated loading range. Once again the average heat of adsorption of CH₄ for CS-H₂O has shifted to above that of CS-CO₂ (approximately + 1 kJ/mol).

Thus, from Figures 3a and 3b it is clear that two adsorbents with very close adsorption uptakes can exhibit vastly different gas-solid interactions. Whilst CS-CO₂ shows energetic heterogeneity for the adsorption of CO₂ and CH₄, CS-H₂O acts homogeneously.

The significantly higher adsorption enthalpy of CO₂ corroborates that carbon dioxide interacts with CS-CO₂ and CS-H₂O much more than CH₄, in agreement with the pure component adsorption isotherms.

From an engineering point of view, the heat of adsorption is a measure of the energy required to regenerate an adsorbent as it provides an indication of the temperature variations that might be expected on the bed during adsorption (and desorption) under adiabatic conditions. Therefore, although high adsorption energies are associated with high selectivities, it is generally desirable for the strongly adsorbed component to have a relatively low adsorption enthalpy in order to reduce the regeneration requirements.

It can also be noticed that there is agreement between our estimations of Q_{st} and the values reported in the literature for CO₂ and CH₄ adsorption on activated carbons [55, 69].

3.4 SELECTIVITY FOR SEPARATING CO₂ FROM CO₂/CH₄ MIXTURES

The selectivity or separation factor (the preferred term in engineering) is another important parameter for evaluating adsorbents. To obtain reliable values it should be estimated from multicomponent (binary in the present case) adsorption data instead of being assessed from pure component adsorption data, which is the more common practice. Selectivity for a binary mixture of CO₂ and CH₄ may be defined by equation 9, where x refers to the molar fraction in the adsorbed phase, estimated, in our case, from the multicomponent IAST-Sips model (it was selected because of its better prediction) and where y refers to the molar fraction in the gas phase (50/50 vol.%). The separation factor is the key for the screening of

adsorbents for use in a PSA process, since, the higher the separation factor is, the greater the purity of the product [71].

$$\text{---} \quad (9)$$

Figure 4 shows the selectivities estimated for both CS adsorbents at three temperatures (303, 323 and 343 K) and over the 0 to 1000 kPa pressure range.

Figure 4. IAST selectivities for CS- CO_2 (solid lines) and CS- H_2O (dashed lines) at 303 (red), 323 (blue) and 343 K (green) up to 1000 kPa for a CO_2/CH_4 (50/50 vol.%) binary mixture.

As can be seen in the figure, selectivity is inversely proportional to temperature. The highest selectivity for both samples is observed at the lowest temperature, 303 K. An increase in temperature reduces the adsorption levels of both gases but increases the gas diffusion of both CO_2 and CH_4 . On the other

hand, small variations in adsorption selectivity with pressure can be observed. It is worth to note that at 303 K selectivity slightly increases with pressure. This behavior may not be accounted for by the non-idealities occurring in the gas phase with increasing pressure. The separation factor increases similarly as the partial loading of carbon dioxide, namely with increasing pressure, decreasing temperature and increasing mole fraction of carbon dioxide in the gas mixture. Apparently a high separation factor exists in conjunction with a high partial loading of carbon dioxide on the adsorbents [29].

Small differences between both adsorbents are observed: CS-H₂O presents a greater selectivity than CS-CO₂ at low pressures at the three temperatures studied but at 1000 kPa the difference in the selectivities of both carbons is less noticeable.

According to these results the maximum selectivity for separating CO₂ as estimated from the adsorption of binary CO₂/CH₄ (50/50) is reached at 303 K and 1000 kPa: 4.3 for CS-CO₂ and 4.4 for CS-H₂O. These values are significantly higher than those reported for carbon adsorbents under similar conditions. *Dreisbach et al.* reported a selectivity of around 2.7 for a mixture of 42% CO₂ on AC Norit R1 Extra at 298 K [31]; *Peng et al.* a selectivity of around 2 for a 50% CO₂ mixture on mesocarbon microbeads at 298 K [72]; *Shao et al.* reported values of around 2.3 for a mixture of 30% CO₂ on activated carbon beads at 298 K [35], while *Kumiawan et al.* obtained a selectivity of approximately 3 for a 50% CO₂ mixture on carbon slit-shaped pores at 318 K [73].

3.5 WORKING CAPACITY

The performance of a PSA unit is not only dictated by the separation factor since this does not reflect the cyclic PSA process. For this reason, another important parameter to be assessed is the working capacity, which is the difference between the amount adsorbed at high pressures and the amount adsorbed at the lowest purge pressure, here assumed to be 100 kPa. The higher the working capacity is, the higher the productivity, i.e., the larger the amount of feed that can be treated with a given amount of adsorbent within a given period of time. This parameter must be estimated under conditions relevant to the separation process and so in this work the binary adsorption equilibrium data from the IAST-Sips model have been used. Figure 5 compares the working capacities for CS-CO₂ and CS-H₂O at the three studied temperatures (303, 323 and 343 K) over the 100 to 1000 kPa pressure range.

Figure 5. IAST working capacities for CS-CO₂ (solid lines) and CS-H₂O (dashed lines) at 303 (red), 323 (blue) and 343 K (green) up to 1000 kPa for a CO₂/CH₄ (50/50 vol.%) binary mixture.

The working capacities are directly correlated to the pressure and inversely correlated to the temperature as might be expected for an adsorption process. The maximum working capacities are then reached at 303 K assuming a pressure of 1000 kPa: 2.8 mmol/g for CS-CO₂ and 2.6 mmol/g for CS-H₂O. Thus, in terms of working capacity CS-CO₂ provides a slightly better performance than CS-H₂O.

3.6 SCREENING THE BEST ADSORBENT

A set of parameters associated with the equilibrium of adsorption were analyzed and evaluated for the two cherry stone-based activated carbons. The results show that no one parameter by itself is valid for identifying the best adsorbent for the specific application under study, CO₂/CH₄ separation. Thus it is necessary to establish a simple method for evaluating and comparing adsorbents based on readily available adsorption data so as to be able to make an appropriate initial selection of adsorbents upon which more extensive tests can be carried out. The ideal adsorbent must have a high selectivity, a high capacity and a low adsorption enthalpy. Therefore, selection of the adsorbent(s) will often involve a compromise between two or more of the above factors, and this makes it all more difficult to compare the adsorbents. For a preliminary evaluation based on equilibrium adsorption data it is useful to define a parameter as simply as possible. For this purpose, the following adsorption performance indicator (*API*), which

balances the three aforementioned parameters (selectivity, $S_{1/2}$, working capacity, WC , and isosteric heat of adsorption, Q_{st}) has been estimated [74]:

$$API = \frac{(S_{1/2}-1)^A WC_1^B}{|Q_{st,1}|^C} \quad (10)$$

In equation 10 the subscript 1 indicates the most adsorbed species, in our case, CO_2 . The isosteric heat of adsorption of the strong adsorbate, $Q_{st,1}$ is in the denominator because the heat generated during adsorption is detrimental to the performance of the process. In order to be able to adapt the API to each separation process, exponents were added so as to be able to adjust the relative importance of each factor. By default, all of the exponents (A , B and C) are set to 1 and they can then be refined based on the objectives of the separation process. For example, for bulk separations the working capacity is of greater importance, whereas for purifications, involving the removal of small amounts of component 1, $S_{1/2}$ is of prime importance. In this work, the primary aim is bulk removal so the exponent for the working capacity (B) has been set to 2 while the rest of the exponents (A and C) have been set to 1. The adsorbent performance indicator has been calculated for each adsorbent using the average of the isosteric heat of adsorption obtained from the Clausius-Clapeyron equation. The values of the parameters together with the estimations of the API values are listed in Table 4.

Table 4. Selectivity, CO₂ Working Capacity, average CO₂ Adsorption Enthalpy, API indicator, and selection parameter *S*, for the CS adsorbents

	Temperature (K)	S_{CO_2/CH_4}	WC, CO ₂ (mol/kg)	Q_{st} , CO ₂ (kJ/mol)	API	<i>S</i>
CS-CO ₂	303	4.35	2.83	21.15	1.27	3.61
	323	3.26	2.39		0.61	2.51
	343	3.01	2.09		0.42	2.26
CS-H ₂ O	303	4.39	2.60	23.03	1.00	3.62
	323	3.55	2.18		0.53	2.78
	343	3.10	1.79		0.29	2.33

The most promising performance corresponds to the adsorbent with the highest calculated *API* for all the evaluated temperatures. So, as can be seen in Table 4, this indicator suggests that CS-CO₂ is the preferred adsorbent and is likely to perform better than CS-H₂O. Other authors, however, have established selection parameters according to the equilibrium adsorption capacities [75]:

$$S = \frac{WC_1}{WC_2} S_{1/2} \quad (11)$$

where WC_1 and WC_2 are the working capacities of the most and least adsorbed components, respectively, and $S_{1/2}$ is the selectivity of component 1 over component 2. This selection parameter has a serious drawback in that it cannot be adapted to account for different objectives in a given process, for instance, depending on whether the principal requirement is high purity or bulk separation.

The values of the selection parameter *S*, listed in Table 4, indicate that there is not a preferred CS sorbent for the CO₂/CH₄ separation, contrary to what the *API* results suggest. Thus, it appears that the incorporation of the heat of adsorption to the analysis of the equilibrium performance of the adsorbents is of critical importance for the selection of the adsorbent for a specific application.

4. CONCLUSIONS

Two low-cost cherry stone-based adsorbents, CS-CO₂ and CS-H₂O, were evaluated for the separation of CO₂ from a 50/50 vol.% CO₂/CH₄ mixture, representative of a biogas stream. For this purpose a systematic study based on the evaluation of the parameters that strongly influence the equilibrium of adsorption was undertaken. Experimental single gas adsorption isotherms for CO₂ and CH₄ at three different temperatures (303, 323 and 343 K) over a pressure range of 0 to 1000 kPa were recorded gravimetrically and fitted to the Sips and Toth models. IAST in conjunction with the Sips and Toth equations was used to predict binary adsorption equilibrium data that were validated with experimental breakthrough adsorption tests for a mixture of CO₂/CH₄ (50/50 vol.%) at 303K and 300 kPa. The isosteric heats of adsorption of CO₂ and CH₄ were evaluated, given the great importance of evaluating this parameter under conditions relevant to the separation, and good agreement to those reported in the literature for activated carbons was found. The CS carbons showed a more enhanced selectivity for separating CO₂ compared to other carbons in the literature evaluated under similar conditions. The adsorption performance indicator (API) showed to be the most adequate indicator and pointed out the importance of the heat of adsorption in the screening of adsorbents for particular applications. Despite the great similarities of both CS carbons in terms of adsorption capacities, CS-CO₂ showed higher performance indicator values than CS-H₂O, suggesting that it would be a more promising activated carbon for the separation of CO₂ from a CO₂/CH₄ mixture typical of biogas streams.

580

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588 **References**

- 589 [1] R.T. Yang, *Adsorbents. Fundamentals and applications.*, John Wiley & Sons, New Jersey, 2003.
- 590 [2] T. Werpy, G. Petersen, *Top Value Added Chemicals from Biomass: Volume I -- Results of*
- 591 *Screening for Potential Candidates from Sugars and Synthesis Gas*, in: *Other Information: PBD: 1*
- 592 *Aug 2004, 2004*, pp. Medium: ED; Size: 76 pp. pages.
- 593 [3] K. Morishige, *Adsorption and Separation of CO₂/CH₄ on Amorphous Silica Molecular Sieve*, *The*
- 594 *Journal of Physical Chemistry C*, 115 (2011) 9713-9718.
- 595 [4] S. Cavenati, C.A. Grande, A.E. Rodrigues, *Separation of mixtures by layered pressure swing*
- 596 *adsorption for upgrade of natural gas*, *Chemical Engineering Science*, 61 (2006) 3893-3906.
- 597 [5] M.D. Rad, S. Fatemi, S.M. Mirfendereski, *Development of T type zeolite for separation of CO₂*
- 598 *from CH₄ in adsorption processes*, *Chemical Engineering Research and Design*, 90 (2012) 1687-
- 599 1695.
- 600 [6] D.D. Iarikov, P. Hacıoğlu, S.T. Oyama, *Supported room temperature ionic liquid membranes*
- 601 *for CO₂/CH₄ separation*, *Chemical Engineering Journal*, 166 (2011) 401-406.
- 602 [7] A. Ghofri, L. Gaberova, J. Rouquerol, D. Vincent, P.L. Llewellyn, G. Maurin, *Adsorption of CO₂,*
- 603 *CH₄ and their binary mixture in Faujasite NaY: A combination of molecular simulations with*
- 604 *gravimetry–manometry and microcalorimetry measurements*, *Microporous and Mesoporous*
- 605 *Materials*, 119 (2009) 117-128.
- 606 [8] S. Rasi, J. Lantela, A. Veijanen, J. Rintala, *Landfill gas upgrading with countercurrent water*
- 607 *wash*, *Waste Management*, 28 (2008) 1528-1534.
- 608 [9] A.G. Chmielewski, A. Urbaniak, K. Wawryniuk, *Membrane enrichment of biogas from two-stage*
- 609 *pilot plant using agricultural waste as a substrate*, *Biomass and Bioenergy*, 58 (2013) 219-228.
- 610 [10] L. Deng, M.-B. Hägg, *Techno-economic evaluation of biogas upgrading process using CO₂*
- 611 *facilitated transport membrane*, *International Journal of Greenhouse Gas Control*, 4 (2010) 638-
- 612 646.
- 613 [11] P. Shao, M. Dal-Cin, A. Kumar, H. Li, D.P. Singh, *Design and economics of a hybrid membrane–*
- 614 *temperature swing adsorption process for upgrading biogas*, *Journal of Membrane Science*, 413–
- 615 414 (2012) 17-28.
- 616 [12] K. Maqsood, A.H. Ali, A.B.M. Shariff, S. Ganguly, *Techno-economic evaluation of cryogenic*
- 617 *networks for separation of CO₂ from natural gas*, in: *Applied Mechanics and Materials*, 2014, pp.
- 618 635-638.
- 619 [13] K. Maqsood, J. Pal, D. Turunawarasu, A.J. Pal, S. Ganguly, *Performance enhancement and*
- 620 *energy reduction using hybrid cryogenic distillation networks for purification of natural gas with*
- 621 *high CO₂ content*, *Korean Journal of Chemical Engineering*, 31 (2014) 1120-1135.
- 622 [14] X. Li, J. Li, B. Yang, *Design and control of the cryogenic distillation process for purification of*
- 623 *synthetic natural gas from methanation of coke oven gas*, *Industrial and Engineering Chemistry*
- 624 *Research*, 53 (2014) 19583-19593.
- 625 [15] Y.-S. Bae, K.L. Mulfort, H. Frost, P. Ryan, S. Punathanam, L.J. Broadbelt, J.T. Hupp, R.Q. Snurr,
- 626 *Separation of CO₂ from CH₄ Using Mixed-Ligand Metal–Organic Frameworks*, *Langmuir*, 24 (2008)
- 627 8592-8598.
- 628 [16] G.D. Pirngruber, L. Hamon, S. Bourrelly, P.L. Llewellyn, E. Lenoir, V. Guillermin, C. Serre, T. Devic,
- 629 *A method for screening the potential of MOFs as CO₂ adsorbents in pressure swing adsorption*
- 630 *processes*, *ChemSusChem*, 5 (2012) 762-776.
- 631 [17] A. Alonso-Vicario, J.R. Ochoa-Gómez, S. Gil-Río, O. Gómez-Jiménez-Aberasturi, C.A. Ramírez-
- 632 *López*, J. Torrecilla-Soria, A. Domínguez, *Purification and upgrading of biogas by pressure swing*
- 633 *adsorption on synthetic and natural zeolites*, *Microporous and Mesoporous Materials*, 134 (2010)
- 634 100-107.

635 [18] R.T. Yang, Gas separation by adsorption processes, Butterworths, Boston, 1987.

636 [19] L. Bastin, P.S. Brcia, E.J. Hurtado, J.A.C. Silva, A.E. Rodrigues, B. Chen, A microporous metal-

637 organic framework for separation of CO₂/N₂ and CO₂/CH₄ by fixed-bed adsorption, Journal of

638 Physical Chemistry C, 112 (2008) 1575-1581.

639 [20] V. Finsy, L. Ma, L. Alaerts, D.E. De Vos, G.V. Baron, J.F.M. Denayer, Separation of CO₂/CH₄

640 mixtures with the MIL-53(Al) metal-organic framework, Microporous and Mesoporous Materials,

641 120 (2009) 221-227.

642 [21] Y.S. Bae, R.Q. Snurr, Development and evaluation of porous materials for carbon dioxide

643 separation and capture, Angewandte Chemie - International Edition, 50 (2011) 11586-11596.

644 [22] M. Tagliabue, D. Farrusseng, S. Valencia, S. Aguado, U. Ravon, C. Rizzo, A. Corma, C.

645 Mirodatos, Natural gas treating by selective adsorption: Material science and chemical engineering

646 interplay, Chemical Engineering Journal, 155 (2009) 553-566.

647 [23] S. Cavenati, C.A. Grande, A.E. Rodrigues, C. Kiener, U. Mller, Metal organic framework

648 adsorbent for biogas upgrading, Industrial and Engineering Chemistry Research, 47 (2008) 6333-

649 6335.

650 [24] M.W. Ackley, S.U. Rege, H. Saxena, Application of natural zeolites in the purification and

651 separation of gases, Microporous and Mesoporous Materials, 61 (2003) 25-42.

652 [25] Q. Wang, J. Luo, Z. Zhong, A. Borgna, CO₂ capture by solid adsorbents and their applications:

653 current status and new trends, Energy & Environmental Science, 4 (2011) 42-55.

654 [26] Y. Li, H. Yi, X. Tang, F. Li, Q. Yuan, Adsorption separation of CO₂/CH₄ gas mixture on the

655 commercial zeolites at atmospheric pressure, Chemical Engineering Journal, 229 (2013) 50-56.

656 [27] J.A.C. Silva, A.F. Cunha, K. Schumann, A.E. Rodrigues, Binary adsorption of CO₂/CH₄ in

657 binderless beads of 13X zeolite, Microporous and Mesoporous Materials, 187 (2014) 100-107.

658 [28] J. Yang, R. Krishna, J. Li, J. Li, Experiments and simulations on separating a CO₂/CH₄ mixture

659 using K-KFI at low and high pressures, Microporous and Mesoporous Materials, 184 (2014) 21-27.

660 [29] E. Buss, Gravimetric measurement of binary gas adsorption equilibria of methane-carbon

661 dioxide mixtures on activated carbon, Gas Separation & Purification, 9 (1995) 189-197.

662 [30] A. Ahmadpour, K. Wang, D.D. Do, Comparison of Models on the Prediction of Binary

663 Equilibrium Data of Activated Carbons, AIChE Journal, 44 (1998) 740-752.

664 [31] F. Dreisbach, R. Staudt, J.U. Keller, High Pressure Adsorption Data of Methane, Nitrogen,

665 Carbon Dioxide and their Binary and Ternary Mixtures on Activated Carbon, Adsorption, 5 (1999)

666 215-227.

667 [32] R. Van Der Vaart, C. Huiskes, H. Bosch, T. Reith, Single and Mixed Gas Adsorption Equilibria of

668 Carbon Dioxide/Methane on Activated Carbon, Adsorption, 6 (2000) 311-323.

669 [33] V. Goetz, O. Pupier, A. Guillot, Carbon dioxide-methane mixture adsorption on activated

670 carbon, Adsorption, 12 (2006) 55-63.

671 [34] P. Ning, F. Li, H. Yi, X. Tang, J. Peng, Y. Li, D. He, H. Deng, Adsorption equilibrium of methane

672 and carbon dioxide on microwave-activated carbon, Separation and Purification Technology, 98

673 (2012) 321-326.

674 [35] X. Shao, Z. Feng, R. Xue, C. Ma, W. Wang, X. Peng, D. Cao, Adsorption of CO₂, CH₄, CO₂/N₂

675 and CO₂/CH₄ in novel activated carbon beads: Preparation, measurements and simulation, AIChE

676 Journal, 57 (2011) 3042-3051.

677 [36] C.A. Grande, F.V.S. Lopes, A.M. Ribeiro, J.M. Loureiro, A.E. Rodrigues, Adsorption of off-gases

678 from steam methane reforming (H₂, CO₂, CH₄, CO and N₂) on activated carbon, Separation

679 Science and Technology, 43 (2008) 1338-1364.

680 [37] S. Sircar, T.C. Golden, M.B. Rao, Activated carbon for gas separation and storage, Carbon, 34

681 (1996) 1-12.

- [38] A.y.M.A. Ministerio de Agricultura, Avance anuario de estadística ministerio de agricultura, alimentación y medio ambiente 2014, in: G.d. España (Ed.), 2015.
- [39] O. Ioannidou, A. Zabaniotou, Agricultural residues as precursors for activated carbon production-A review, *Renewable and Sustainable Energy Reviews*, 11 (2007) 1966-2005.
- [40] M. Olivares-Marín, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, Preparation of activated carbon from cherry stones by chemical activation with ZnCl₂, *Applied Surface Science*, 252 (2006) 5967-5971.
- [41] M. Olivares-Marín, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, Preparation of activated carbons from cherry stones by activation with potassium hydroxide, *Applied Surface Science*, 252 (2006) 5980-5983.
- [42] M. Olivares-Marín, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, Porous Structure of Activated Carbon Prepared from Cherry Stones by Chemical Activation with Phosphoric Acid, *Energy & Fuels*, 21 (2007) 2942-2949.
- [43] M. Olivares-Marín, V. Del Prete, E. Garcia-Moruno, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, The development of an activated carbon from cherry stones and its use in the removal of ochratoxin A from red wine, *Food Control*, 20 (2009) 298-303.
- [44] M. Olivares-Marín, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, Adsorption of mercury from single and multicomponent metal systems on activated carbon developed from cherry stones, *Adsorption*, 14 (2008) 601-610.
- [45] J. Jaramillo, V. Gómez-Serrano, P.M. Álvarez, Enhanced adsorption of metal ions onto functionalized granular activated carbons prepared from cherry stones, *Journal of Hazardous Materials*, 161 (2009) 670-676.
- [46] U. Beker, B. Ganbold, H. Dertli, D.D. Gülbayir, Adsorption of phenol by activated carbon: Influence of activation methods and solution pH, *Energy Conversion and Management*, 51 (2010) 235-240.
- [47] L. Lakov, P. Vassileva, O. Peshev, Sorption of heavy metals on pyrazolone-containing carbon sorbents, *Carbon*, 37 (1999) 1655-1657.
- [48] D. Angin, Utilization of activated carbon produced from fruit juice industry solid waste for the adsorption of Yellow 18 from aqueous solutions, *Bioresource Technology*, 168 (2014) 259-266.
- [49] M. Olivares-Marín, J.A. Fernández, M.J. Lázaro, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, F. Stoeckli, T.A. Centeno, Cherry stones as precursor of activated carbons for supercapacitors, *Materials Chemistry and Physics*, 114 (2009) 323-327.
- [50] J.C. Arrebola, A. Caballero, L. Hernán, J. Morales, M. Olivares-Marín, V. Gómez-Serrano, Improving the performance of biomass-derived carbons in li-ion batteries by controlling the lithium insertion process, *Journal of the Electrochemical Society*, 157 (2010) A791-A797.
- [51] A. Caballero, L. Hernán, J. Morales, Limitations of disordered carbons obtained from biomass as anodes for real lithium-ion batteries, *ChemSusChem*, 4 (2011) 658-663.
- [52] S. Himeno, T. Komatsu, S. Fujita, Development of a new effective biogas adsorption storage technology, *Adsorption*, 11 (2005b) 899-904.
- [53] S. Himeno, T. Komatsu, S. Fujita, High-pressure adsorption equilibria of methane and carbon dioxide on several activated carbons, *Journal of Chemical and Engineering Data*, 50 (2005a) 369-376.
- [54] M.-B. Kim, Y.-S. Bae, D.-K. Choi, C.-H. Lee, Kinetic Separation of Landfill Gas by a Two-Bed Pressure Swing Adsorption Process Packed with Carbon Molecular Sieve: Nonisothermal Operation, *Industrial & Engineering Chemistry Research*, 45 (2006) 5050-5058.
- [55] C.A. Grande, A.E. Rodrigues, Biogas to Fuel by Vacuum Pressure Swing Adsorption I. Behavior of Equilibrium and Kinetic-Based Adsorbents, *Industrial & Engineering Chemistry Research*, 46 (2007) 4595-4605.

- [56] D.D. Do, Adsorption analysis: equilibria and kinetics, Imperial College Press, London, 1998.
- [57] D.M. Ruthven, Principles of adsorption and desorption processes, John Wiley & Sons, New York, 1984.
- [58] S. García, J.J. Pis, F. Rubiera, C. Pevida, Predicting mixed-gas adsorption equilibria on activated carbon for precombustion CO₂ capture, *Langmuir*, 29 (2013) 6042-6052.
- [59] N. Álvarez-Gutiérrez, M.V. Gil, F. Rubiera, C. Pevida, Cherry stones-based activated carbons as potential adsorbents for CO₂/CH₄ separation: Effect of the activation parameters, *Greenhouse Gases: Science and Technology*, 5 (2015) 1-14.
- [60] C.F. Martín, S. García, D. Beneroso, J.J. Pis, F. Rubiera, C. Pevida, Precombustion CO₂ capture by means of phenol-formaldehyde resin-derived carbons: From equilibrium to dynamic conditions, *Separation and Purification Technology*, 98 (2012) 531-538.
- [61] F. Dreisbach, H.W. Lösch, P. Harting, Highest Pressure Adsorption Equilibria Data: Measurement with Magnetic Suspension Balance and Analysis with a New Adsorbent/Adsorbate-Volume, *Adsorption*, 8 (2002) 95-109.
- [62] S. García, M.V. Gil, C.F. Martín, J.J. Pis, F. Rubiera, C. Pevida, Breakthrough adsorption study of a commercial activated carbon for pre-combustion CO₂ capture, *Chemical Engineering Journal*, 171 (2011) 549-556.
- [63] M.V. Gil, N. Álvarez-Gutiérrez, M. Martínez, F. Rubiera, C. Pevida, A. Morán, Carbon adsorbents for CO₂ capture from bio-hydrogen and biogas streams: Breakthrough adsorption study, *Chemical Engineering Journal*, 269 (2015) 148-158.
- [64] A.L. Myers, J.M. Prausnitz, Thermodynamics of mixed-gas adsorption, *AIChE Journal*, 11 (1965) 121-127.
- [65] W. Rudziński, K. Nieszporek, H. Moon, H.K. Rhee, On the theoretical origin and applicability of the potential theory approach to predict mixed-gas adsorption on solid surfaces from single-gas adsorption isotherms, *Chemical Engineering Science*, 50 (1995) 2641-2660.
- [66] J. Juliš, Differential heats of adsorption, *Chemical Papers*, 29 (1975) 653-659.
- [67] J.A. Dunne, R. Mariwala, M. Rao, S. Sircar, R.J. Gorte, A.L. Myers, Calorimetric heats of adsorption and adsorption isotherms. 1. O₂, N₂, Ar, CO₂, CH₄, C₂H₆, and SF₆ on silicalite, *Langmuir*, 12 (1996) 5888-5895.
- [68] D.G. Hartzog, S. Sircar, Sensitivity of PSA process performance to input variables, *Adsorption*, 1 (1995) 133-151.
- [69] I.A.A.C. Esteves, M.S.S. Lopes, P.M.C. Nunes, J.P.B. Mota, Adsorption of natural gas and biogas components on activated carbon, *Separation and Purification Technology*, 62 (2008) 281-296.
- [70] D.P. Valenzuela, A.L. Myers, O. Talu, I. Zwiebel, Adsorption of gas mixtures: effect of energetic heterogeneity, *AIChE Journal*, 34 (1988) 397-402.
- [71] D.M. Ruthven, S. Farooq, K.S. Knaebel, Pressure Swing Adsorption, VCH Publishers, New York, 1994.
- [72] X. Peng, W.C. Wang, R.S. Xue, Z.M. Shen, Adsorption separation of CH₄/CO₂ on mesocarbon microbeads: Experiment and modeling, *AIChE Journal*, 52 (2006) 994-1003.
- [73] Y. Kurniawan, S.K. Bhatia, V. Rudolph, Simulation of binary mixture adsorption of methane and CO₂ at supercritical conditions in carbons, *AIChE Journal*, 52 (2006) 957-967.
- [74] A.D. Wiersum, J.S. Chang, C. Serre, P.L. Llewellyn, An adsorbent performance indicator as a first step evaluation of novel sorbents for gas separations: Application to metal-organic frameworks, *Langmuir*, 29 (2013) 3301-3309.
- [75] S.U. Rege, R.T. Yang, A simple parameter for selecting an adsorbent for gas separation by pressure swing adsorption, *Separation Science and Technology*, 36 (2001) 3355-3365.