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Evaluation of the Performance of an Activated Carbon's family for Biogas Upgrading using the Adsorption Performance Indicator

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Abstract

The ideal selection of adsorbents for a wide range of binary gas separations remains a critical challenge, but the combining of the primary key adsorption parameters, including adsorption capacity, selectivity, and heat of adsorption using the adsorption performance indicator (API), facilitates this selection. The study applies the API to choose the selective adsorbent for separating CO₂ from an equimolar CO₂/CH₄ mixture, representing a biogas stream. Three activated carbons (ACs) of the CNR family (CNR-115, CNR-115-ox, and CNR-115-ox-am) are discussed, highlighting their ability to selectively adsorb the carbon dioxide molecules while preserving the valuable methane component. Also, the heat of adsorption of CO₂ indicated that the three ACs are regenerative as they are in the range of physisorption. The addition of chemical groups on the surface of the ACs plays an essential role in varying the adsorption parameters. Although the three ACs belong to the same family, it was shown that the addition of the different chemical surfaces and varying the pressure changes the choice of the ideal adsorbent; CNR-115-ox showed a better overall performance than the others under the low-pressure region (< 1.5 MPa) due to the presence of oxygen groups, but CNR-115-ox-am is the preferred one for the separation of CO₂ from CO₂/CH₄ mixtures under the high-pressure region due to the presence of nitrogen groups.

Keywords: Biogas, Adsorption, Activated carbon, Adsorption performance indicator, Carbon dioxide

Introduction

The extensive use of fossil fuels in recent decades has reached dangerous levels, increasing greenhouse gas (GHG) emissions and, therefore, increasing global warming. Thus, they must be transitioned to renewable and sustainable

sources to reduce environmental issues^[1]. Bioenergy, particularly biogas produced via anaerobic digestion of biomass wastes, is considered a viable alternative energy source^[2]. It is a mixture of gases, composed mainly of methane (CH₄) (40-75% v/v) and carbon dioxide (CO₂) (25-55% v/v) with small amounts of other gases such as hydrogen sulfide (H₂S), ammonia (NH₃), water vapor, siloxanes, halogenated hydrocarbons, etc. Removing or reducing the CO₂ content in biogas is essential to maximize its energy content and make it suitable for various applications, such as natural gas grid, and fuel for vehicles^[3]. Various methods have been employed for biogas upgrading to separate the CO₂ content, including pressure swing adsorption (PSA), absorption, membrane separation, cryogenic upgrading, and biological separation^[4]. Among the techniques above, PSA is one of the commonly used methods for biogas upgrading; the mechanism behind the PSA involves the affinity and interaction between the CO₂ molecules and the solid's surface under varying pressure conditions. A wide variety of adsorbents have been used to separate CO₂ from biogas mixtures, such as ACs, silica gels, metal-organic frameworks, zeolites, biochars, carbon nanotubes, and carbon molecular sieves^{[3][5]}. The essential characteristics of the ACs that attracted researchers to choose them for CO₂ adsorption are their excellent chemical and thermal stability, thermal conductivity, less impact to the presence of water, high surface area (up to 4000 m² g⁻¹), wide presence of micropores, and availability of low-cost precursors^[3]. ACs can be engineered to have greatly varying properties that increase CO₂ adsorption and selectivity for CO₂ over CH₄ by enhancing their physico-chemical properties^[6]. Many studies have been conducted on increasing the surface basicity of the ACs to improve the adsorption of the CO₂ pure gas and the separation of the CO₂/CH₄ mixture due to the Lewis acid behavior of CO₂ molecules^{[3][7]}. For instance, introducing basic surface functionalities to the ACs presented a high CO₂ adsorption capacity with more than 4.5 mol kg⁻¹ at 0.1 MPa and 298 K under low carbonization and activation conditions^[8]. Similar findings were observed by Khalil *et al.* in which the chemical impregnation of AC with monoethanolamine caused an increase in the adsorption capacity from 18 mg/mg to 49 mg/mg compared to the untreated AC at atmospheric pressure and room temperature.^[9] Regarding the CO₂/CH₄ mixture, Peredo-Mancilla *et al.* observed that the selectivity ($S_{(CO_2/CH_4)}$) showed the highest value on the AC treated chemically with oxygen and ammonia due to the increased presence of basic surface^[7].

In this context, the present work aims to evaluate and compare the adsorption performance of the studied ACs based on a new indicator called "Adsorption Performance Indicator," which comprises the three adsorption parameters (heat of adsorption, working capacity, and selectivity of the CO₂/CH₄ from an equimolar mixture)^[10]. The latter two factors were already determined and published by Peredo *et al.*^[7].

Materials and experimental apparatuses

Materials

Three ACs of the CNR family have been selected for comparative analysis: one commercial (CNR-115) and two modified (CNR-115-ox and CNR-115-ox-am). The commercial AC Norit CNR-115 was purchased from Cabot

Corporation company in France which has been modified to improve its efficiency for biogas separation processes. The chemical treatment of commercial CNR-115 was carried out in two successive steps at the Mulhouse Materials Science Institute (IS2M) in France, as shown in Figure 1: CNR-115 was oxidized in air at 400°C for 2 hours to increase the amount of oxygenated groups, followed by ammonium vapor (NH_4OH) treatment at 25°C (298K) for 36 hours to increase the amount of nitrogen groups^[7].

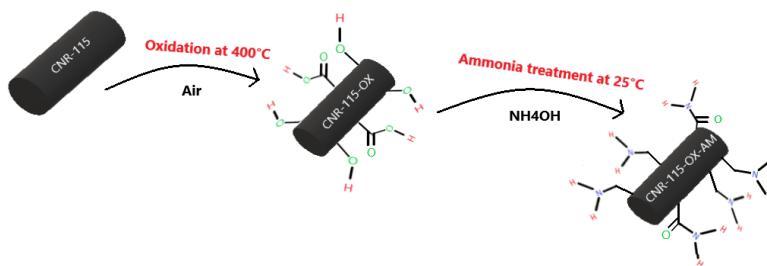


Figure 1: Chemical treatments of the commercial activated carbon CNR-115

Physicochemical Characterization

The textural and chemical characteristics of the three samples were obtained at the Mulhouse Materials Science Institute (IS2M) and the Laboratory of Complexes Fluids and their Reservoirs (LFCR) of University of Pau and Pays de l'Adour (UPPA) in France and already published by Peredo-Mancilla *et al.*^[7].

It can be seen from Table 1 that all the texture properties of the commercial AC decrease after the two-step chemical modifications. The oxidation step significantly decreased the surface area from 1714 to 929 $\text{m}^2 \text{g}^{-1}$ due to the treatment with an oxidizing agent, which may be attributed to the formation of carbon-oxygen complexes on the surface. Also, the treatment of the oxidized AC with the ammonia vapor decreased the surface area to 352 $\text{m}^2 \text{g}^{-1}$ because the additional nitrogen groups block some pores. Also, the average pore size becomes narrower by passing from 1.1 nm for CNR-115 to 0.78 nm for CNR-115-ox-am. Regarding the chemical characteristics, the oxidation step leads to an increase in the total oxygen-containing groups (such as carboxyls and alcohols) with a value of 1.29 mmol g^{-1} compared to the commercial CNR-115 (0.49 mmol g^{-1}), this result is consistent with lowering the pH_{pzc} of commercial CNR-115 from 6.14 to 5.87. However, the ammonia treatment promoting the formation of basic surface groups, that can be observed in the increase of the pH_{pzc} from 5.87 to 6.48.

High-pressure differential scanning calorimeter

The heat of adsorption of CO_2 into the ACs was calculated by integrating the adsorption capacity of CO_2 from the adsorption isotherms and the heat involved, which was measured using a high-pressure differential scanning calorimeter (micro DSC VII from Setaram). The minimum temperature that this calorimeter can reach is about -45°C , and the maximum temperature is 120°C thanks to Peltier thermoelectric devices, with uncertainty estimated at 0.2 K. The calorimetric block is composed of two cells; the measurement and reference cells (Figure 2), which are gas-tight

Table 1: Texture properties and Acid/Basic Oxygenated Surface Groups Content of the CNR's family^[7]

Activated carbon	Texture properties					Chemical properties		
	$S_{BET}(m^2 g^{-1})$	$V_{micro}(cm^3 g^{-1})$	$V_{meso}(cm^3 g^{-1})$	$L_0(nm)$	pH_{pzc}	Total acid ($mmol g^{-1}$)	Total basic ($mmol g^{-1}$)	
CNR-115	1714	0.64	0.31	1.10	6.14	0.49	0.61	
CNR-115-ox	929	0.36	0.09	0.96	5.87	1.39	0.46	
CNR-115-ox-am	352	0.14	0.07	0.78	6.48	1.15	1.20	

Standard deviation: $\sigma pH = 0.04$, $\sigma acid = 0.003 mmol g^{-1}$, $\sigma basic = 0.003 mmol g^{-1}$

high-pressure cells made of stainless steel. The samples are accurately weighed (≈ 70 mg) before being introduced into the measurement cell. First, to remove any fluid particles contained in the system, a regeneration process takes place by subjecting the sample to a couple of vacuum (10^{-2} Pa) (through the gas panel) and heating at a temperature of $90^\circ C$ for 24 h. Afterward, the temperature in the furnace, which contains both cells, is cooled down from $90^\circ C$ to $30^\circ C$ at a scanning rate of $1 K min^{-1}$. It is kept at this temperature (temperature of study) during the overall adsorption process to ensure uniform temperature distribution and stabilization of the heat flow signals. A quantity of pure gas (CO_2) is introduced and regulated through the gas panel to the calorimetry until the required pressure is reached.

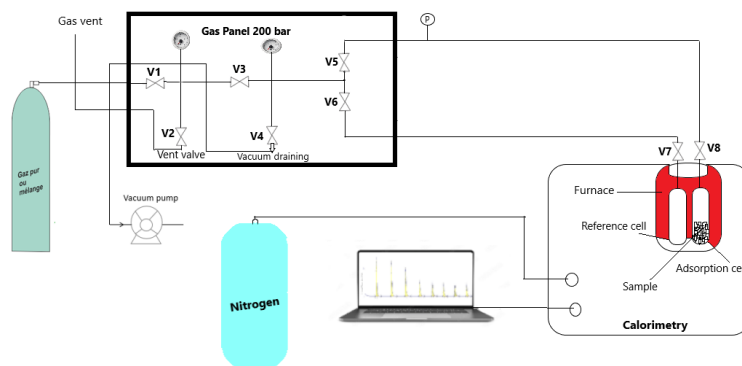


Figure 2: Schematic of the calorimeter "micro DSC VII"

Determination of Adsorption Performance Indicator(API)

The separation of a constituent from a gas mixture using adsorbents is based on three primary parameters: the selectivity, the adsorption capacity, and the heat of adsorption. Thus, these latter parameters solely can't describe the performance of the different materials in separating a mixture of gases. Therefore, for the primary selection of the adsorbents for a specific separation process, a single indicator called "Adsorption Performance Indicator" was proposed by Wiersum *et al.* to combine the three parameters mentioned above with different relative importance of each one depending on the objectives of the study^[10]. An adsorbent that has a higher selectivity and adsorption capacity together with a lower heat of adsorption is considered the ideal material for biogas separation, but it is rare to

find one that combines these three properties at the same time. The following form can present the API relation:

$$API = \frac{(S_{1/2} - 1)^A WC_1^B}{|\Delta H_{ads,1}|^C} \quad (1)$$

In equation 1, $S_{1/2}$ is the selectivity of component 1 over component 2, WC_1 is the working capacity of the stronger adsorbate component 1, and $\Delta H_{ads,1}$ is the heat of adsorption of component 1 which takes place in the denominator of the relation because it is detrimental to the performance of the process. A, B, and C are the exponents of the selectivity, the working capacity and the heat of adsorption, respectively.

Results and discussions

Heat of adsorption

The heat of adsorption indicates the interaction strength between the adsorbed gas and the adsorbent surface, which explains the ACs' affinity to the gas molecules. Figure 3 shows the heat of adsorption calculated by combining the results of the adsorption isotherms of the CO₂ pure gas and the calorimetry measurements of the CO₂ adsorption into the CNR family at 30 °C as a function of pressure. It was shown that the calculated heat of adsorption for all the ACs studied varied in the range of physisorption (<40 kJ mol⁻¹); hence, a reversible adsorption process is expected^[11]. The heat of adsorption of CNR-115, CNR-115-ox, and CNR-115-ox-am decreases from 14.95 ± 0.67, 26.78 ± 0.45, and 28.08 ± 0.26 kJ mol⁻¹ to 10.01 ± 0.10, 23.29 ± 0.27, and 24.57 ± 1.64 kJ mol⁻¹, respectively in a corresponding pressure range of 0.1 – 2.4 MPa. For all the ACs, the heat of adsorption is high in the low-pressure region due to the strong interaction between CO₂ molecules and the favorable active sites of the ACs (monolayer adsorption). As pressure increases, the heat of adsorption typically begins to decrease from its initial high value because more CO₂ molecules are adsorbed onto the AC's surface, and the surface sites become occupied by CO₂, weakening the interactions between adsorbent and adsorbate. At a certain point, when most of the available adsorption sites are filled (monolayer coverage), the heat of adsorption reaches a plateau in which an additional pressure increase does not significantly alter the heat of adsorption. For the ACs, CNR-115-ox and CNR-115-ox-am, at very high pressures, the heat of adsorption increased due to the electrostatic interactions between CO₂ and the chemical functional groups on the material's surface. The heat of adsorption of CO₂ on commercial AC (unmodified) is often lower than on chemically modified AC because it primarily relies on physical adsorption mechanisms, such as Van Der Waals forces and these interactions are generally weak. Regarding the regeneration energy requirements, CNR-115-ox-am and CNR-115-ox require higher energy to break the strong adsorbate-adsorbent interactions and desorb the CO₂ molecules but the dominance of the physisorption range can mean that the CNR-115-ox-am is still regenerable^[7].

Adsorption isotherms

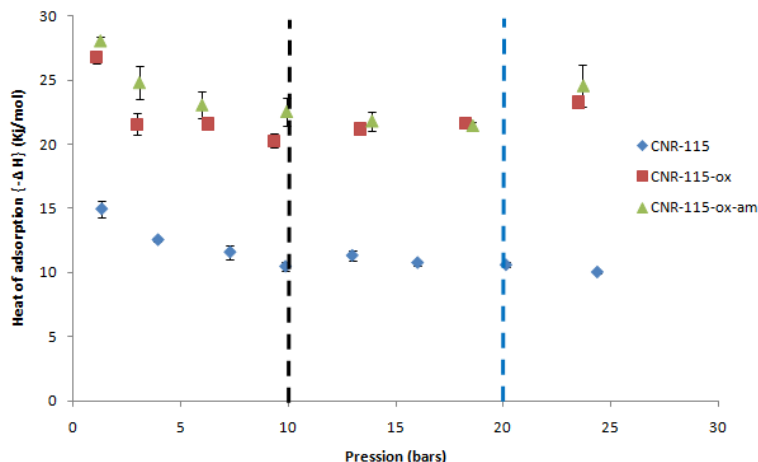


Figure 3: Heat of adsorption of the activated carbons of the CNR115 family at 30 °C K as a function of pressure

This part includes the data obtained of the equimolar CH_4/CO_2 separation into the ACs's family by Peredo *et al.* for the adsorption capacity and the selectivity at 30 °C and 1 and 2 MPa as shown in Table 2^[7]. We noted that the three samples had a higher adsorption uptake of CO_2 than CH_4 mainly due to the large quadrupole moment of CO_2 and the non-polarity of CH_4 ^[12]. It was observed that the adsorption of CO_2 in the oxidized CNR-115-ox is higher than in the unmodified sample (CNR-115) due to the presence of oxygen functionalities of groups, which induce the formation of hydrogen bonds between CO_2 and the carbon surface. However, this adsorption capacity decreased after the ammonia treatment due to the pore blockage by the presence of the new nitrogen surface groups as shown in Table 1. The adsorption capacity of CH_4 is more related to the texture properties of the ACs; it increased with increasing the porosity; thus, the CH_4 uptake is higher in the commercial carbon than the two modified samples due to the decrease of the surface area and pore volume after the modification and it is negligible in the CNR-115-ox-am as a result of its basic character. Regarding the selectivity, which is the preferential adsorption of CO_2 over CH_4 , it was seen that the three ACs had a high selectivity as it is more than 1. At 2 MPa, the selectivity ($S_{\text{CO}_2/\text{CH}_4}$) showed the highest value on the CNR-115-ox-am ($\sim 102 \pm 1.02$) compared to the two other ACs due to the presence of basic surface on the modified carbon, which enhances the CO_2 adsorption capacity with a negligible CH_4 adsorption.

Table 2: Adsorption parameters for the separation of CO_2/CH_4 mixture into the ACs used at 30 °C and at the two pressures 1 and 2 MPa

	1 MPa			2 MPa		
	CNR-115	CNR-115-ox	CNR-115-ox-am	CNR-115	CNR-115-ox	CNR-115-ox
CO_2 adsorption capacity (mol kg^{-1})	3.05 ± 0.03	3.2 ± 0.03	1.9 ± 0.02	3.9 ± 0.04	4.4 ± 0.04	2.6 ± 0.03
CH_4 adsorption capacity (mol kg^{-1})	1.7 ± 0.02	0.85 ± 0.008	0.2 ± 0.002	2.9 ± 0.03	1.4 ± 0.014	0
Selectivity $S_{(\text{CO}_2/\text{CH}_4)}$	2.6 ± 0.03	17.2 ± 0.17	9.1 ± 0.09	1.4 ± 0.01	10.1 ± 0.1	102 ± 1.02
Heat of adsorption of CO_2 (kJ mol^{-1})	11.45 ± 0.36	20.62 ± 0.46	22.5 ± 1.02	11.56 ± 0.2	22.3 ± 0.24	22.7 ± 1.1

Adsorption Performance indicator

In this study, API is used to evaluate the performance of the three adsorbents for removing CO₂ molecules from CH₄ molecules. In this regard, we give higher importance to the parameter "adsorption capacity" with an exponent "B=2", but the exponents (A and C, see equation 1) of the two remaining parameters are kept to 1. Figure 4(a) presents the API variation as a pressure function. API results indicate that the ideal adsorbent differs by varying the pressure; under the low-pressure region (< 1.5 MPa), the adsorbent CNR-115-ox has the highest values with a maximum of 15.74 ± 0.48 at 1.25 MPa, which means that the presence of oxygen groups enhances the separation of CO₂/CH₄ in this region. However, by increasing the pressure above 1,5 MPa, API suggests that CNR-115-ox-am is the preferred adsorbent with a maximum value of 40.27 ± 1.69 at 2.25 MPa and is likely to perform much better than the two other adsorbents. This is due to its higher selectivity under this pressure region, thanks to the electrostatic interactions between the CO₂ molecules and the basic nitrogen surface. Figure 4(b) shows the API values of each adsorbent at the two pressures 1 and 2 MPa; at 1 MPa, the adsorbent CNR-115-ox has the highest value (8.05 ± 0.24) compared to the other two adsorbents as a result of the presence of oxygen groups. However, the scenario was changed at 2 MPa; CNR-115-ox-am is the ideal adsorbent with a value of 30.08 ± 1.5 due to the presence of the basic nitrogen surface. Also, it is clear from Table 2 that the sequence order of the heat of adsorption of CO₂, the working capacity of CO₂ and the selectivity of CO₂ over CH₄ on these adsorbents are not correspond to the order of the API values. This demonstrates the significance of the API indicator in screening adsorbents for binary gas separations.

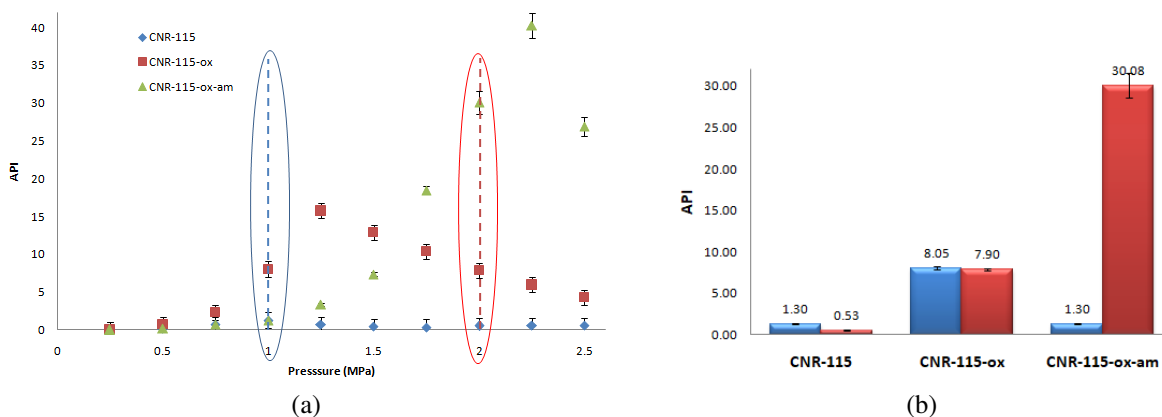


Figure 4: (a) API variation as a function of pressure. (b) API values of the CNR Family at 1 MPa (Blue) and 2 MPa (Red).

Conclusion

Three ACs of the CNR family, one commercial (CNR-115) and two modified (CNR-115-ox and CNR-115-ox-am) were used to evaluate their performance on separating the equimolar CO₂/CH₄ mixture at 30 °C K. The evaluation of this performance was done using the Adsorption Performance Indicator, which integrated the three main adsorption parameters: the heat of adsorption in which the three samples are within the range of physisorption, but the modified carbons have higher values due to the chemical interactions with the CO₂ molecules. The CO₂ working capacity

in which the oxidized CNR-115-ox has the highest values due to the presence of the oxygen groups, the selectivity ($S(\text{CO}_2/\text{CH}_4)$) in which the more selective is the CNR-115-ox-am at higher pressure due to the chemical interaction of the CO_2 molecules with the basic surface, with a negligible CH_4 adsorption. Finally, API results indicate that the adsorbent CNR-115-ox is preferred over the two other adsorbents under the low-pressure region as a result of the presence of the oxygen surface groups, but CNR-115-ox-am is the most promising carbon material above 1.5 MPa due to its higher selectivity as a result of the presence of the nitrogen functional groups.

References

- (1) ABBASI, T.; ABBASI, S. A. Is the Use of Renewable Energy Sources an Answer to the Problems of Global Warming and Pollution? *Critical Reviews in Environmental Science and Technology* **2012**, *42*, 99–154.
- (2) Guo, M.; Song, W.; Buhain, J. Bioenergy and biofuels: History, status, and perspective. *Renewable and Sustainable Energy Reviews* **2015**, *42*, 712–725.
- (3) Abd, A. A.; et al. A review on application of activated carbons for carbon dioxide capture: present performance, preparation, and surface modification for further improvement. *Environmental Science and Pollution Research* **2021**, *28*, 43329–43364.
- (4) Petersson, A.; Wellinger, A. Biogas upgrading technologies – developments and innovations. 2010.
- (5) Abd, A. A.; Naji, S. Z.; Hashim, A. S.; Othman, M. R. Carbon dioxide removal through physical adsorption using carbonaceous and non-carbonaceous adsorbents: A review. *Journal of Environmental Chemical Engineering* **2020**, *8*, 104142.
- (6) Bedia, J.; Peñas-Garzón, M.; Gómez-Avilés, A.; Rodríguez, J. J.; Belver, C. A Review on the Synthesis and Characterization of Biomass-Derived Carbons for Adsorption of Emerging Contaminants from Water. *C* **2018**, *4*, 63.
- (7) Peredo-Mancilla, D.; et al. Surface-Modified Activated Carbon with a Superior CH_4/CO_2 Adsorption Selectivity for the Biogas Upgrading Process. *Industrial & Engineering Chemistry Research* **2022**, *61*, 12710–12727.
- (8) To, J. W. F. e. a. Hierarchical N-Doped Carbon as CO_2 Adsorbent with High CO_2 Selectivity from Rationally Designed Polypyrrole Precursor. *Journal of the American Chemical Society* **2016**, *138*, 1001–1009.
- (9) Khalil, S. H.; Aroua, M. K.; Daud, W. M. A. W. Study on the improvement of the capacity of amine-impregnated commercial activated carbon beds for CO_2 adsorbing. *Chemical Engineering Journal* **2012**, *183*, 15–20.
- (10) Wiersum, A. D.; Chang, J.-S.; Serre, C.; Llewellyn, P. L. An Adsorbent Performance Indicator as a First Step Evaluation of Novel Sorbents for Gas Separations: Application to Metal-Organic Frameworks. *Langmuir* **2013**, *29*, 3301–3309.
- (11) Rashidi, N. A.; Yusup, S.; Lam, H. L. Kinetic Studies on Carbon Dioxide Capture using Activated Carbon. *Chemical Engineering Transactions* **2013**, *35*, 361–366.
- (12) Álvarez Gutiérrez, N.; Gil, M. V.; Rubiera, F.; Pevida, C. Adsorption performance indicators for the CO_2/CH_4 separation: Application to biomass-based activated carbons. *Fuel Processing Technology* **2016**, *142*, 361–369.