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Performance of a vine shoots-derived activated carbon during dynamic adsorption of CO₂ in dry and humid conditions

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PURPOSE OF THE ABSTRACT

Removing CO₂ from low-pressure flue gas (i.e., CO₂ capture in postcombustion) has been the focus of extensive research over the last 30 years. As an alternative to the energy-intensive amine-based chemical absorption processes, CO₂ capture via adsorption on renewable biomass-derived carbons has recently gained increased interest, since these adsorbents are relatively cheap, require low energy for regeneration, and show a relatively good tolerance to moisture existing in flue gas [1]. An increasing number of previous studies have focused on producing activated carbons (ACs) from different biomass precursors. However, a major part of these studies has been limited to equilibrium uptake measurements. For this reason, there is a need to test the ability of biomass-derived ACs under dynamic conditions. In this study, we investigated the performance of a physically activated vine shoots-derived biochar to separate CO₂ from N₂/CO₂ binary mixtures (in dry and humid conditions) via multicycle breakthrough (BT) measurements.

Biochar was first produced by slow pyrolysis of vine shoots under N₂ flow at 500 °C in a packed bed reactor [2]. The obtained solid material was then physically activated at 800 °C under a steady flow of CO₂ in N₂ (20/80 vol. %). Under these conditions, a holding time of 1 h resulted in a burn-off of approximately 22 wt. %. Textural properties of the resulting AC were estimated from N₂ and CO₂ adsorption isotherms at -196 and 0 °C, respectively, using a Micromeritics ASAP 2020. Adsorption isotherms of both pure components at 25 and 50 °C were also measured. The apparent selectivity CO₂/N₂ was calculated according to Hao et al. [3]. Table 1 reports the most important parameters deduced from the above-mentioned measurements.

Cyclic BT tests at 25 and 50 °C were performed in a stainless steel fixed-bed column (20.9 mm ID). 15.1 g of AC (which was previously degassed) was packed into the column, leading to a bed height of 22 cm. Dynamic adsorption was then measured by feeding a flow containing CO₂ and N₂ (14-15 vol. % of CO₂) at 110 kPa and a total flow rate of 0.22 L (STP) min⁻¹. The gas residence time within the bed was 12.2-13.2 s, which is notably lower than those used in previous studies [4]. For dynamic experiments under humid conditions, a steady flow of water was fed using a HPLC pump. The adsorption stage was continued until saturation, where the outlet concentration of CO₂ (measured using a continuous gas analyzer ABB) reaches the value at the inlet. Afterwards, the bed was regenerated using a vacuum pump at an absolute pressure of 20 kPa under a flow of N₂.

Fig. 1 shows the obtained breakthrough curves (5 cycles) in dry conditions at 25 and 50 °C. It can be seen that the performance at 25 °C was more than acceptable, in terms of breakthrough time, stability, and CO₂ uptake, which was 0.87 ± 0.09 mmol g⁻¹ (75 ± 1.9 % until BT time). This value was quite close to that of equilibrium,

indicating a relatively fast kinetics. Furthermore, the apparent selectivity CO₂/N₂ was 45 ± 7.4 , considerably higher than the value reported in Table 1. As expected, the CO₂ uptake at 50 °C decreased to 0.50 ± 0.02 mmol g⁻¹ (69 ± 1.7 % until BT time). The apparent selectivity CO₂/N₂ (29 ± 1.1) was in this case more similar to that estimated from adsorption isotherms.

Under humid conditions at 50 °C, the adsorbent exhibited good stability (after 10 cycles), considerably adsorption capacities (0.47 ± 0.06 mmol g⁻¹), and an outstanding apparent selectivity (138 ± 44.0). However, the observed BT times were shorter than those measured at dry conditions, leading to a marked decrease in the CO₂ uptake until BT time (30 ± 2.2 %). This result suggests that a higher adsorption pressure and/or a longer gas residence time could be required for a proper adsorption of CO₂ in the presence of moisture.

FIGURES

Table 1. Textural properties, adsorption capacity and apparent selectivity deduced from adsorption isotherms.

Apparent specific surface area (m ² g ⁻¹)		Specific pore volume (cm ³ g ⁻¹) ^a					Temperature (°C)	CO ₂ uptake at 15 kPa (mmol g ⁻¹)	Apparent selectivity CO ₂ /N ₂ (-)
<i>S_{BET}^b</i>	<i>S_{BET}^c</i>	<i>V_t</i>	<i>V_{mic}</i>	<i>V_{mes}</i>	<i>V_{ultra}</i>				
397	349	0.189	0.147	0.027	0.135	25	1.05	28	
						50	0.61	26	

^a The total pore volume (*V_t*) was determined from the N₂ adsorption isotherm at -196 °C at a relative pressure of 0.98–0.99. The t-plot method was used to estimate the micropore volume (*V_{mic}*). A Non-Local Density Functional Theory (NLDFT) method assuming slit-pore geometry was used to estimate the Pore Size Distribution. The mesopore volume (*V_{mes}*) was then calculated as the difference between the cumulative pore volume for a pore width of 50 nm and *V_{mic}*. The ultra-micropore volume (*V_{ultra}* for pore sizes lower than 0.7 nm) of carbons were estimated from the CO₂ adsorption isotherm at 0 °C using a Density Functional Theory (DFT) method (slit-pore geometry).

^b calculated from N₂ adsorption data at -196 °C.

^c calculated from CO₂ adsorption data at 0 °C.

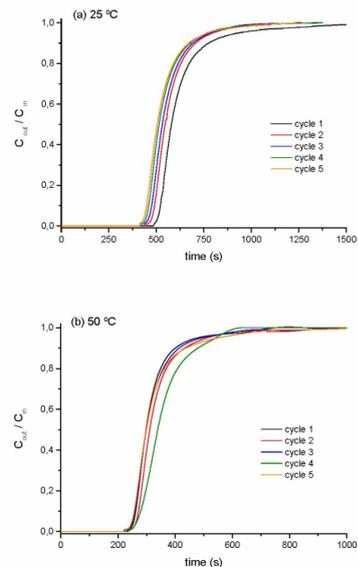


Figure 1. CO₂ breakthrough curves in dry conditions at 25 °C (a) and 50 °C (b).

FIGURE 1

Table 1

Textural properties, adsorption capacity and apparent selectivity deduced from adsorption isotherms

FIGURE 2

Fig. 1

CO₂ breakthrough curves in dry conditions at 25 °C (a) and 50 °C (b)

KEYWORDS

CO₂ capture in postcombustion | biomass-derived activated carbon | breakthrough curves | dry and humid conditions

BIBLIOGRAPHY

- [1] J.J. Manyà, B. González, M. Azuara, G. Arner, Ultra-microporous adsorbents prepared from vine shoots-derived biochar with high CO₂ uptake and CO₂/N₂ selectivity, *Chem. Eng. J.* 345 (2018) 631–639. doi:10.1016/j.cej.2018.01.092.
- [2] M. Azuara, E. Sáiz, J.A. Manso, F.J. García-Ramos, J.J. Manyà, Study on the effects of using a carbon dioxide atmosphere on the properties of vine shoots-derived biochar, *J. Anal. Appl. Pyrolysis* 124 (2017) 719–725. doi://doi.org/10.1016/j.jaap.2016.11.022.
- [3] W. Hao, F. Björnerbäck, Y. Trushkina, M. Oregui Bengoechea, G. Salazar-Alvarez, T. Barth, N. Hedin, High-Performance Magnetic Activated Carbon from Solid Waste from Lignin Conversion Processes. 1. Their Use As Adsorbents for CO₂, *ACS Sustain. Chem. Eng.* 5 (2017) 3087–3095. doi:10.1021/acssuschemeng.6b02795.
- [4] S. Shahkarami, A.K. Dalai, J. Soltan, Y. Hu, D. Wang, Selective CO₂ Capture by Activated Carbons: Evaluation of the Effects of Precursors and Pyrolysis Process, *Energy Fuels* 29 (2015) 7433–7440. doi:10.1021/acs.energyfuels.5b00470.