CO_2 separation by adsorption with biomass-based carbon adsorbents activated with $ZnCl_2$ and H_3PO_4

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Separation or purification processes employed for gaseous streams continue to be of great importance in the chemical industry, both for the purification of streams of interest, such as upgrading energy vectors, and for preventing the emission of pollutant gases. One of the most applied operations for carrying out these separation processes is gas-liquid absorption technology, either using physical or chemical absorbents. Although it is a widely used technique that achieves satisfactory separation results, certain negative aspects have generated interest in alternative separation operations, such as the use of membranes or adsorption (Abuelnoor *et al*., 2007). These negative aspects mainly focus on issues related to corrosion caused by chemical solvents and the high energy costs mainly associated with the regeneration of these solvents.

When chemical absorption processes are used for gas purification, the choice of solvent is very important as it affects the kinetics of the process and the equipment size. In the same way, the use of adsorption operations for gas separation implies the appropriate selection of the adsorbent material that plays a key role. In this case, factors such as adsorption capacity and selectivity must be considered to achieve a suitable separation result. A significant number of solids have been screened for gases adsorption, yielding results of great interest. Particularly, certain molecular organic frameworks have stood out, but at the same time, they have shown certain negative aspects that limit their industrial application in addition to the significant cost associated with their synthesis (Xiao *et al*., 2024).

The conclusions reached in previous studies (i.e. Serafin *et al*., 2017) were focussed on the role of pore size in gas adsorption. The important role of pores with small size was stablished and it allows progress in the manufacturing of adsorbents with characteristics that can enhance the adsorption capacity and/or the selectivity. Nevertheless, it is difficult to establish such specific characteristics. Al-Sakkari *et al*. (2023) concluded that specific surface areas greater than 450 m^2/g, accompanied by pore volume above 0.5 cm^3/g and small pore sizes (less than 4.4 Å), tend to generate adsorbents with promising performance. However, in the case of activated carbon production, it is challenging to fully meet these recommendations because this type of material typically has a broad pore size distribution.

For all these reasons, this work proposes the development and improvement of carbonaceous-type adsorbents derived of waste materials from the food industry. In this study, two types of biomass wastes, commonly found in agricultural activities around the Mediterranean zone, were used: olive pits and almond shells. These precursors were subjected to an initial carbonization stage (at 600 ºC) and a subsequent activation process at 850ºC with phosphoric acid (H_3PO_4) or zinc chloride ($ZnCl_2$), using 1:2 or 1:4 (g/g) carbon:activating agent ratios.

Table 1 shows information regarding the porous structure characteristics of the adsorbents, such as specific surface area and volume generated by the porous structure. An overall analysis of the fabricated carbons revealed that there are no important differences in surface area, or pore volume and furthermore, all carbons presented a high degree of microporosity (always above 90%) after activation, which was one of the goals pursued with the use of these activating agents. Specifically, the O_$ZnCl_2$_4 carbon achieved the highest surface area along with the greatest degree of microporosity, being both characteristics of significant interest for gas separation processes via adsorption operation.

Regarding the smallest pore range within microporosity, known as ultramicroporosity (pore diameters smaller than 7 Å), a decrease in the presence of this type of pores is observed in all cases after the activation treatment. The non-activated carbons exhibited ultramicroporosity degrees of 76.3% and 72.7% for almond shell and olive pit, respectively (Rahimi *et al*, 2025). On the other hand, carbons activated using $ZnCl_2$ showed a greater pore volume in this size range, which is of interest, as previously discussed.

Carbon dioxide adsorption isotherms have been determined for the different adsorbents fabricated, and Table 1 shows the adsorption capacity obtained at two different pressures (15 and 101.3 kPa) to evaluate these adsorbents with gas streams containing low concentrations of CO_2. In general, it can be observed that the carbons activated using $ZnCl_2$ show higher adsorption capacities, both at low and high pressures. This behaviour could be

clearly related to the presence of a greater number of small-sized pores, that as previously discussed can enhance carbon dioxide adsorption (Al-Sakkari *et al*., 2023). Moreover, the greatest enhancement corresponds to the carbons made from olive pits and activated with $ZnCl_2$.

Table 1. Characteristics of porous structure and CO_2 adsorption data for adsorbents used in the present work.

Carbon	SSA* (m^2/g)	V_{total} * (cm^3/g)	MP* (%)	UMP (%)	$q_{(15\ kPa)}$ (cm^3/g)	$q_{(101.3\ kPa)}$ (cm^3/g)	$S_{(101.3\ kPa)}$ (-)
A_H_3PO_4_2	833.1	0.412	92.8	53.1	18.3	55.6	143
A_H_3PO_4_4	791.2	0.388	93.5	58.0	18.0	54.8	451
A_$ZnCl_2$_2	635.5	0.300	90.6	69.1	19.6	54.1	145
A_ $ZnCl_2$_4	719.6	0.327	94.4	67.2	19.2	55.7	134
O_H_3PO_4_2	714.9	0.352	93.5	60.1	19.2	55.5	244
O_H_3PO_4_4	711.8	0.351	92.9	59.0	18.3	53.6	338
O_ $ZnCl_2$_2	712.0	0.328	90.5	65.8	19.4	55.5	184
O_ $ZnCl_2$_4	849.5	0.377	97.7	65.5	20.2	61.8	116

A: almond shell; O: olive stone; 2: carbon:KOH ratio = 1:2 (g/g); 4: carbon:KOH ratio = 1:4 (g/g); SSA: specific surface area; V_{total}: total pore volume; MP: microporosity; UMP: ultramicroporosity, q: adsorption capacity determined at 25 ºC; S: CO_2 selectivity estimated by Ideal Adsorption Solution Theory. * Rahimi *et al*, 2025.

As before mentioned, the selection of adsorbents for gas stream separation/purification should not only focus on the amount of gas adsorbed but also on adsorption selectivity, which allow achieving high purity in the treated streams. In this way, selectivity data have been determined from the adsorption isotherms for carbon dioxide and nitrogen using the Ideal Adsorption Solution Theory (IAST) at a pressure of 101.3 kPa (Table 1). The obtained data for carbon dioxide selectivity shows an opposite behaviour to that previously described for adsorption capacity. For both precursors, the adsorbents that showed the highest selectivity for carbon dioxide separation were those activated with H_3PO_4. Therefore, it seems that smaller pore sizes may enhance adsorption but not selectivity. As previously discussed, it is difficult to assign specific importance to the characteristics of an adsorbent for gas separation processes.

Therefore, in relation to selectivity, it appears that the characteristics of the porous structure alone cannot explain the experimental behaviour observed. In addition to these characteristics, surface chemistry may play an important role in the interactions between adsorbate and adsorbent. A previous study (Rahimi *et al*., 2025) showed that activation processes with H_3PO_4 produces adsorbents with higher oxygen content (between 30% and 40% more). This higher oxygen content may be related to functional groups generated in the activation process, which could contribute to the higher selectivity in the adsorption of carbons made using H_3PO_4.

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