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Calorimetric study of activated carbons impregnated with CaCl_2

Abstract: Activated carbon monoliths with different surface characteristics were prepared by impregnating oil palm stone with diluted aqueous CaCl_2 solutions (with concentrations between 2 and 7% w/v) without binders. The solids were characterized by determination of nitrogen adsorption isotherms at 77 K and carbon dioxide adsorption isotherms at 273 K using volumetric adsorption equipment. Surface area and micropore volume values were calculated from the nitrogen isotherms using the BET and DR models, respectively, obtaining solids with low percentages of mesoporosity. Immersion enthalpies of the activated carbon monoliths were determined in benzene, with values between -173 and -104 J g⁻¹, and water, with values between 61 and 30 J g⁻¹, indicating that the monoliths have a hydrophobic character.

Keywords: activated carbon monoliths, CaCl_2 impregnation, N_2 adsorption, CO_2 adsorption, immersion enthalpies

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1 Introduction

Porous materials such as molecular sieves, zeolites and activated carbons, due to their highly developed porous structure, are suitable materials for capturing gases e.g. CO_2 or CH_4 [1,2]. Activated carbons typically have a high porous structure, which confers a large surface area and high pore volume when compared with other porous solids. These characteristics make these materials excellent adsorbents in gas- as well as liquid-phase processes.

Activated carbons have also other important advantages such as versatility in manufacturing, i.e. the ability to modify their porous structure and surface chemistry based on the requirements in a particular application, the ability to easily modify their conformation (dust, grain, cloth, etc.), the ability to recover the adsorbate, and easy regeneration of the material, etc. Applications of activated carbons in a gas-phase constitute about 20% of their global use. The main applications are gas-phase vapour recovery in gasoline cars, retention of industrial gases that are toxic pollutants or cause odours, air conditioning systems, gas masks, and catalyst support, etc. [3,4].

The production of activated carbon is related to product purification and environmental protection. As the demand for product purity requires ever more sophisticated processes and emission standards become more stringent, activated carbon technology also progresses, the classical granular and powdered forms being supplanted or extended to other forms such as fibres, and fabrics, etc. Monoliths offer the opportunity to adjust the distribution of the porosity or the chemical nature of the surface, or can be impregnated with chemicals to increase the selectivity of substance removal [5,6].

Studies on forms of activated carbon that are known and currently marketed show that monoliths have characteristics that differ from conventional forms, among which the following are highlighted: they allow the passage of gases with a very small pressure drop, possess a high geometric surface area per unit weight or volume, the gas flow is very uniform, they are easily handled and abrasion resistant, and they have fewer constraints generated by internal diffusion and mass transfer phenomena. Because of the said properties they have become favoured as carriers or adsorbents in direct adsorption processes with gas phase material [7,8]. Activated carbon monoliths have been manufactured from several sources, including wood, coal, peat, and bone nuts, and their adsorption capacities measured with a wide range of organic compounds: polar and aromatic, aliphatic, and non-polar. The synthesis of carbon monoliths, whether used as direct supports or adsorbents, is an alternative approach to environmental issues and an innovative field of research [9].

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2 Materials and methods

2.1 Preparation of activated carbons

Activated carbon monoliths were prepared using Cuesco lignocellulosic African Palm as precursor, which was ground sieved to a particle size of 38 μm . The precursor was impregnated with 2, 3, 5 and 7% w/v solutions of H_3PO_4 and then supplemented to 32% (to facilitate compaction of the monoliths). Impregnation was performed at 358 K for 6 hours and then the temperature was increased to 393 K for about 8 hours. These conditions were selected based on previous work and the literature [10,11]. To produce monoliths of activated carbons a compaction process was conducted in which the precursors previously impregnated chemically were carried to uniaxial press and were subjected to a pressure of 4500 psi and a temperature of 423 K for 30 seconds. The formed monoliths were subjected to heat treatment under a CO_2 flow of 100 mL min^{-1} at a heating rate of 3 K min^{-1} up to 1073 K and is maintained at this temperature for 6 hours. Then heating was performed at 873 K for 2 hours in a N_2 atmosphere to remove excess CO_2 from the materials [12]. The monoliths were initially washed with a diluted solution of 0.01 M HCl, then with distilled water at 333 K, and finally dried in an oven at 383 K for 12 hours and stored in plastic containers and sealed under nitrogen. The designation of the samples was as follows: MC, activated carbon monoliths followed by Ca that correspond to CaCl_2 activating agent, and finally CaCl_2 solution concentration.

2.2 Determination of adsorption isotherms

A textural characterization was performed for carbonaceous materials prepared in this research with of N_2 and CO_2 adsorption isotherms at 77 K and 273 K respectively. To perform these analyses, the samples were first degassed at 473 K for 24 hours. The apparent surface area was calculated from the BET equation. The micropore volume V_o (N_2) and the volume of narrow micropores V_n (CO_2) were obtained by applying the equation of Dubinin-Radushkevich to the adsorption data with nitrogen and carbon dioxide, respectively. The total pore volume V_t is calculated from the volume adsorbed at a relative pressure of 0.99, and the mesopore volume by the difference [13].

2.3 Determining immersion enthalpies of the activated carbon monoliths in benzene and water

To determine enthalpies, about 100 mg of each of the activated carbon monoliths were weighed, placed in a glass vial attached to the calorimetric cell and dipped in 10 mL of benzene. The cell was first placed in the main heat sink and the temperature of the calorimetric set was allowed to stabilise for about 1 hour, or the time required for stabilization of the calorimeter. Then the sample was immersed in the liquid and the resulting thermal changes were recorded until the baseline stabilized again. Finally, a post-period was recorded for 20 min. and the electrical calibration was performed [14].

3 Results and discussion

3.1 Characterization of the materials

Fig. 1 shows the N_2 adsorption isotherms at 77 K of the activated carbon monoliths prepared. It can be noted that materials prepared using calcium chloride solutions as the impregnating agent yielded microporous isotherms of type I according to the classification of the IUPAC [15]. With the increased CaCl_2 concentration a decrease in the adsorption capacity of nitrogen in the materials and in their textural characteristics was observed. This is probably caused by the fact that the narrow porosity of the material is blocked by CaCl_2 .

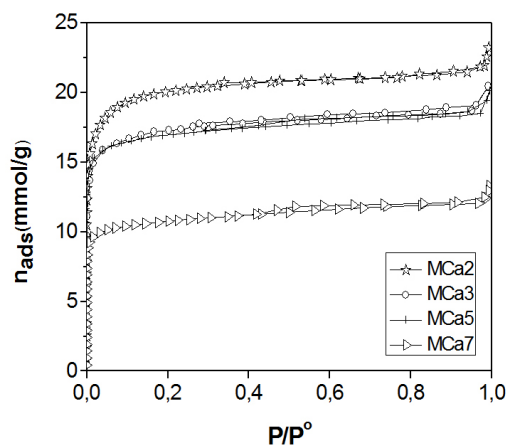
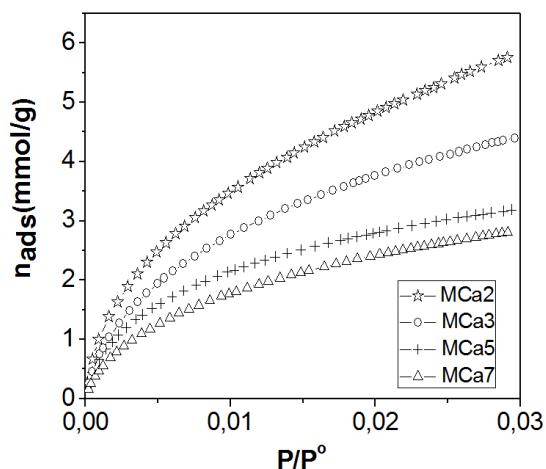
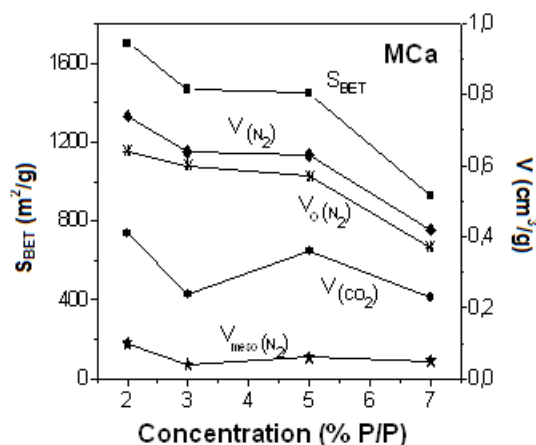


Figure 1: N_2 adsorption isotherms of activated carbon monoliths at 77 K.

Table 1: Surface properties of activated carbon monoliths determined from the adsorption isotherms of N_2 at 77 K and CO_2 at 273 K.

N_2 at 77 K isotherms adsorption						CO_2 at 273 K Adsorption
Monoliths	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_o ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	V_t ($\text{cm}^3 \text{g}^{-1}$)	L_o (nm)	V_n ($\text{cm}^3 \text{g}^{-1}$)
MCCa2	1700	0.64	0.10	0.74	0.98	0.43
MCCa3	1469	0.60	0.04	0.64	1.01	0.34
MCCa5	1445	0.57	0.06	0.63	0.97	0.36
MCCa7	926	0.37	0.05	0.42	0.97	0.23

**Figure 2:** CO_2 adsorption isotherms at 273 K of the activated carbon monoliths.**Figure 3:** Comparison of pore volumes and surface areas of the activated carbon monoliths with increasing CaCl_2 concentration.

The activated carbon monoliths present high surface area values in terms of micropore volume with little development of mesoporosity, with their similar values indicating little influence of the concentration of CaCl_2 during impregnation. The results are presented in Table 1. Narrow microporosity

values varied between 0.43 and 0.23 $\text{m}^2 \text{g}^{-1}$, indicating that the materials have pores with dimensions of about 1.0 nm [16].

The CO_2 adsorption isotherms of the solids are presented in Fig. 2. It is evident that their behaviour in regard to adsorption of the gas is similar to that obtained for N_2 , because with the increase of the concentration of the CaCl_2 solution, the gas adsorption decreases and the values of the textural parameters fall.

The variation in the textural characteristics is presented in Fig. 3 as a function of the concentration of the impregnant (CaCl_2). S_{BET} , V_o and V_n 0.99 decreased with increasing CaCl_2 concentration for all the observed monoliths, while mesopore volumes (V_{meso}) remained almost constant, with a slightly higher value of 0.10 $\text{cm}^3 \text{g}^{-1}$ for the solid obtained with the 2% CaCl_2 solution.

In the preparation of the monoliths, the precursor material is subjected to a process that combines physical and chemical activation. Initially the impregnation of shell with CaCl_2 promotes degradation of lignocellulosic components; thereafter, further additions degrade the H_3PO_4 vegetable matrix, releasing more tar on the surface of the particles than in the case of monoliths facilitating agglomeration of the precursor. Then the reaction of gasification of coal with CO_2 ($\text{C}-\text{CO}_2$), catalysed by Ca [17] was applied to extract carbon atoms from the structure. In the activated carbon obtained this way an increase of the concentration of Ca caused increased removal of carbon atoms from the matrix. In the consequence this led to the growth of the pores and consequently a decrease in the microporosity and surface area.

Immersion enthalpies were obtained with the activated carbon monoliths in benzene and water in order to relate non-specific and specific interactions of the solids with solvents of different polarity. Surface properties and capacities were determined after CO_2 adsorption by these solids. The thermograms obtained with the highest and lowest values of surface area after immersion of the MCCa₂ and MCCa₇ monoliths in benzene are shown in Fig. 4.

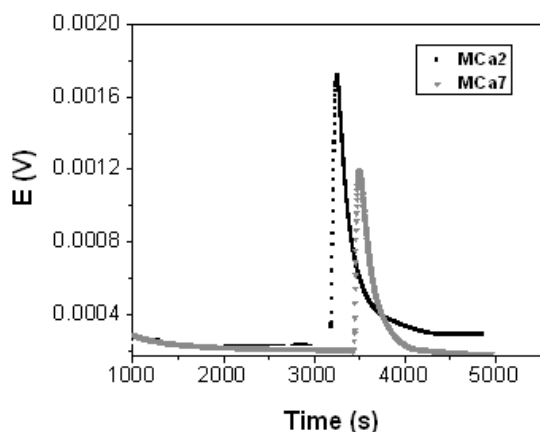


Figure 4: Thermograms obtained by immersing the activated carbon monoliths in benzene.

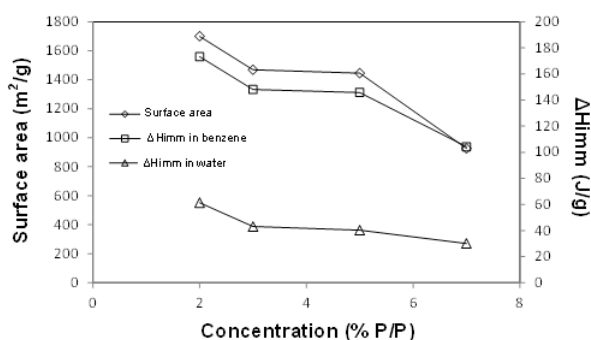


Figure 5: Variation in surface area and enthalpies after immersion of activated carbon monoliths in benzene or water as a function of the concentration of CaCl_2 .

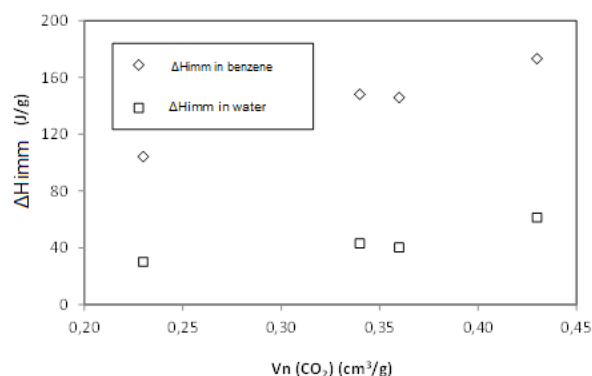


Figure 6: Enthalpies of immersion of activated carbon monoliths in benzene and water based on the volume of narrow micropores.

Immersion enthalpies are proportional to the areas of the peaks in a graph of electrical potential versus time. Values of immersion enthalpy between -104.8 and -173.2 J g^{-1} were obtained, which are comparable to those achieved for microporous solids [18]. The results

Table 2: Enthalpies immersing the monoliths in benzene and water.

Monoliths	$-\Delta H_{\text{imm}} \text{ en } \text{C}_6\text{H}_6$ (J g^{-1})	$-\Delta H_{\text{imm}} \text{ en } \text{H}_2\text{O}$ (J g^{-1})	Hydrophobic factor ($-\Delta H_{\text{imm}} \text{ C}_6\text{H}_6 / -\Delta H_{\text{imm}} \text{ H}_2\text{O}$)
MCa2	-173.2 ± 1.4	-61.35 ± 1.2	2.82
MCa3	-148.1 ± 0.3	-43.06 ± 0.5	3.44
MCa5	-145.8 ± 1.6	-40.27 ± 1.0	3.62
MCa7	-104.2 ± 0.9	-30.03 ± 0.8	3.74

obtained after immersing the activated carbon monoliths in benzene and water and the values for each variant of the hydrophobic solid obtained for the ratio between the enthalpy immersed in benzene and the enthalpy of immersion are shown in Table 2 [19].

The immersion enthalpies of activated carbon monoliths in the two solvents are exothermic. Higher values were obtained for the interaction with benzene, which shows the surface coverage by a solvent with a non-specific interaction.

In preparing the activated carbon monoliths the experimental variable studied was the CaCl_2 concentration used to impregnate the precursor, which resulted in solids being generated with differences in their textural properties. This effect of salt concentration is reflected in the surface area values and enthalpies of the solids after immersion in benzene, as shown in Fig. 5.

An increase in the enthalpy of immersion in benzene with increasing BET area of the carbon materials was observed. This behaviour is consistent with described by Denoyel [20]. In a similar work, carbonaceous materials were prepared and characterized by immersion calorimetry in benzene and carbon tetrachloride, and a proportionality was found between the enthalpy of immersion and the surface area accessible to the immersion liquid [21]. The immersion enthalpies of the solids in benzene and water versus the volume of narrow micropores calculated from the adsorption of CO_2 are presented in Fig. 6.

It can be observed that the values of the enthalpies of solid immersion in both solvents increased with the volume of micropores, making a larger difference for the immersion in benzene, which had a rate of change of 341 J cm^3 , while for immersion in water the rate of change was about half of this value. In both solvents the relation between the enthalpy of immersion and micropore narrow volume is linear; however, a better fit is obtained for immersion in benzene.

The experimental data described earlier was used to calculate the value of the surface area of each solid from its nitrogen absorption using the BET model and its solvent-accessible surface area through determining the

enthalpy of immersion in benzene [21]. The relationship between the CO_2 absorbing capacity of the solids and the surface area values achieved using two different methods is shown in Fig. 7. It was observed that the amount of gas adsorbed is proportional to the surface area, with a linear behaviour that presented a better adjustment to the values obtained for the surface area available to the molecules when benzene was used as the immersion liquid.

4 Conclusions

Four activated carbon monoliths were prepared by soaking seeds in the palm shell with aqueous solutions of calcium chloride (2–7% w/w). Solids were obtained with surface areas up to $1700 \text{ m}^2 \text{ g}^{-1}$ and pore volumes up to $0.74 \text{ cm}^3 \text{ g}^{-1}$, based on N_2 adsorption. The textural parameters such as: surface area, micropore volume and total volume decreased with increasing concentration of the CaCl_2 solution. The mesopore volume remained constant in different salt concentrations. Enthalpies of immersion for the activated carbon monoliths were obtained in benzene and water, with values ranging between -104 and -173 J g^{-1} , and -61 and -30 J g^{-1} , highlighting the hydrophobic character of the monoliths. The immersion enthalpy of solids in two solvents decreased with increasing salt concentration. The adsorption capacity of CO_2 through the monoliths was directly proportional to the surface area of the same.

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