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## CO<sub>2</sub> gas-adsorption calorimetry applied to the study of chemically activated carbons

Débora Aline Soares Maia<sup>1a</sup>, José Carlos Alexandre de Oliveira<sup>1</sup>, Marcelo Sandro Nazzarro<sup>2</sup>, Karim Manuel Sapag<sup>2</sup>, Raul Horácio López<sup>2</sup>, Sebastião Mardônio Lucena<sup>1</sup>, Diana Cristina Silva de Azevedo<sup>1</sup>

Débora Aline Soares Maia<sup>1a</sup>

Email: debora.maia@gpsa.ufc.br

José Carlos Alexandre de Oliveira<sup>1</sup>

E-mail: jcadeoliveira1@gmail.com

Marcelo Sandro Nazzarro<sup>2</sup>

E-mail: nazzarro@gmail.com

Karim Manuel Sapag<sup>2</sup>

E-mail: ksapag@gmail.com

Raul Horácio López<sup>2</sup>

E-mail: lalo.lopez@gmail.com

Sebastião Mardônio Lucena<sup>1</sup>

E-mail: lucena@ufc.br

Diana Cristina Silva de Azevedo<sup>1</sup>

E-mail: diana@gpsa.ufc.br

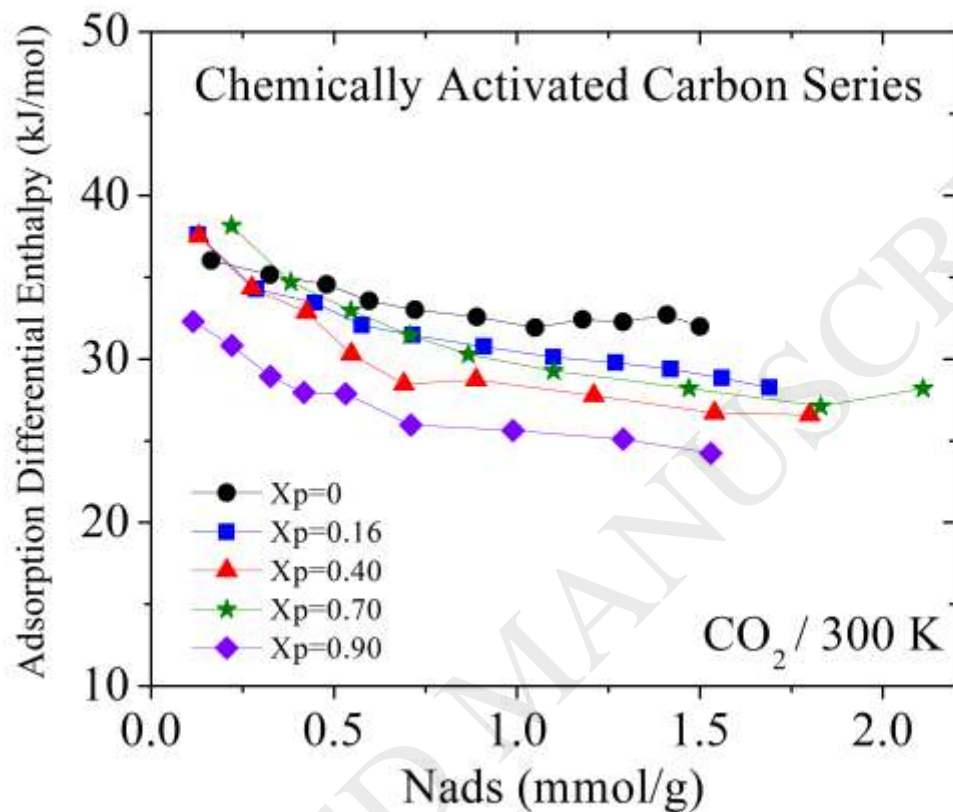
<sup>(1)</sup> Grupo de Pesquisa em Separações por Adsorção (GPSA), Departamento de Engenharia Química, Universidade Federal do Ceará, Campus do Pici – Bloco 731. Fortaleza – Ceará - Brazil

<sup>(2)</sup> Instituto de Física Aplicada (INFAP), Departamento de Física, CONICET-Universidad Nacional de San Luis, Ejército de los Andes 850. San Luis, Argentina

<sup>(a)</sup> debora.maia@gpsa.ufc.br

(a) Corresponding author: debora.maia@gpsa.ufc.br

## Graphical abstract



## Highlights:

- We applied microcalorimetric techniques to a series of chemically activated carbons
- GCMC simulation was used to aid the interpretation of adsorption enthalpy profiles
- We also investigated the existing surface oxygen groups using TPD experiments
- Microcalorimetry measurements allowed discriminating between pore filling regimes

**Abstract**

In this work, the microporous structure of a series of H<sub>3</sub>PO<sub>4</sub> chemically activated carbons from peach stones with increased activation degree were investigated. CO<sub>2</sub> Adsorption equilibrium isotherms and differential enthalpy curves were simultaneously measured at 300 K using a Tian-Calvet microcalorimeter coupled to an adsorption manometric setup.

Temperature programmed decomposition experiments were used to assess density of oxygen functional groups and determine the impact of surface chemistry on CO<sub>2</sub> adsorption capacity. Computer based theoretical calculations were also performed to attempt to predict the adsorption enthalpy profiles. The most activated sample (X<sub>p</sub>=0.90) has an average adsorption enthalpy which is approximately 8 kJ/mol lower than that of the non-activated samples carbonized under the same conditions. The combination of techniques enabled a better understanding of the pore filling regimes with increasing coverage, since the use of CO<sub>2</sub> as a probe gas allows accessing small pores, which otherwise would not be identified from N<sub>2</sub> isotherms at 77 K. The oxygen content on the carbon surface decreased almost 80% with the increasing degree of activation and did not influence in the CO<sub>2</sub> adsorption. Besides providing information about carbon chemistry, CO<sub>2</sub> adsorption calorimetry can also be successfully applied to the screening of carbons intended for CO<sub>2</sub> capture.

**Keywords:** *Activated carbon, adsorption microcalorimetry, PSD*

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## 1. Introduction

Calorimetric methods, with appropriate probe molecules, are especially useful to characterize the chemical nature of surfaces, providing direct and reliable energy data, which is normally required for a complete understanding of the surface phenomena. When applied to the study of the adsorption processes, it has the advantage of revealing useful information about the mechanisms of adsorption (pore filling and phase transitions) (Llewellyn and Maurin, 2005).

In the case of amorphous materials, like activated carbons, calorimetry can help unveil details of the adsorbate-adsorbent interactions in the micropore region (Llewellyn, 2000). It is possible to sense the heterogeneities related to surface chemistry, e.g. oxygenated functional groups, that may change adsorbate-adsorbent interactions, leading to more or less intense heats of adsorption as compared to a pure carbonaceous surface with the same porous texture (Pikunic et al., 2005). Despite these noticeable advantages of calorimetry, the amount of experimental and theoretical work dedicated to the determination of adsorption isotherms far exceeds that dedicated to heats of adsorption. This can be explained by the fact that the

measurement of the heat of adsorption is significantly more difficult and expensive than the measurement of adsorption isotherms (Llewellyn, 2003).

We note that calorimetry has scarcely been directly applied to the issue of investigating the development of microporosity, which is an essential feature in activated carbons for gas adsorption. Most studies in the literature focus on the application of calorimetry in the analysis of carbon chemistry. A typical study was performed by Menendez et al. (Menendez et al., 1996) to explain why H<sub>2</sub>- and N<sub>2</sub>-treated carbons have very different O<sub>2</sub> uptakes. Calorimetry revealed an unexpected high adsorption heat (> 100 kcal/mol) suggesting chemisorption. By matching the heat released by proposed oxygen surface groups, the authors could develop a model to explain the dramatic O<sub>2</sub> adsorption difference. Similar studies were performed by Zarifyanz et al. (Zarifyanz et al., 1967), Davini (Davini, 1993), Rychlicki and Terzyk (Rychlicki and Terzyk, 1995) and Duisterwinkel and Bokhoven (Duisterwinkel and van Bokhoven, 1995) with NO, SO<sub>2</sub>, methane and water respectively. Few studies used calorimetry with CO<sub>2</sub> as probe-molecule. We believe this situation is about to change due to the renewed interest in CO<sub>2</sub> capture. An example is the recent study by Djeridia and co-workers (Djeridi et al., 2016) which correlated N<sub>2</sub> isotherms at 77 K, micropore volume, CO<sub>2</sub> adsorption isotherm and CO<sub>2</sub> microcalorimetric measurements with carbon electrical conductivity.

In this paper, as a contribution to the investigation on microporosity development in activated carbons, we applied calorimetric techniques to a series of chemically activated carbons from peach stones (activated at different H<sub>3</sub>PO<sub>4</sub>/precursor ratios). To the better of our knowledge it was the first time that CO<sub>2</sub> adsorption enthalpy was performed in a complete activated carbon series with increasing development of porosity. Molecular simulation was used to aid the interpretation of adsorption enthalpy profiles and to confirm the proposed adsorption mechanism. In order to measure simultaneously the adsorbed phase concentration and the respective released heat, a manometric setup was coupled to the microcalorimeter (Rouquerol et al., 1999; Sing, 1998). In the experiments, CO<sub>2</sub> at 300 K and 1 bar was used as a probe gas in order to achieve several purposes. CO<sub>2</sub> at 300 K has no diffusivity problems as those found in N<sub>2</sub> at 77 K, in which case a fraction of the pore volume is often inaccessible to characterization (Silvestre-Albero et al., 2012). Also, CO<sub>2</sub> at 300 K interacts strongly with

the activated carbon surface resulting in optimum resolution in the calorimeter signal. Taking advantage of this good resolution, we also investigated the influence of the existing surface oxygen groups on the adsorption of the CO<sub>2</sub> molecule (quadrupolar character), for which purpose temperature programmed decomposition (TPD) experiments were performed. Finally, in view of the great interest of adsorption in CO<sub>2</sub> capture, the temperature and pressure of the experiments were compatible with those found in industrial streams.

## **2. Experimental**

### **2.1 Samples Preparation**

The activated carbon (AC) samples used in this study were prepared by chemical activation with phosphoric acid using peach stones (particle size 2-3 mm) as precursor (Molina-Sabio et al., 1995; Soares Maia et al., 2010). The precursor was impregnated with increasing amounts of phosphoric acid (85% v/v in water). The impregnation degree was defined as the mass ratio between the amount of phosphorus and the amount of precursor,  $X_p$  (grams of phosphorus/grams of precursor) (Prauchner and Rodríguez-Reinoso, 2008). The impregnation was carried out by immersion for two hours at 358 K (Muñoz-González et al., 2009), until complete evaporation of the solution. After impregnation, the samples were submitted to a one-step carbonization in a muffle furnace at 723 K for 2 h (heating rate of 10 K.min<sup>-1</sup>) with no controlled gas flux in air atmosphere. This carbonization temperature has been found to be the optimal one to maximize the development of porosity and achieve high surface area (Molina-Sabio et al., 2003; Rios, R.B. et al., 2009). After carbonization, the samples were rinsed with distilled water up to pH 7 in order to thoroughly remove the remaining phosphoric acid. Finally, the samples were dried at 373 K for 2 h. Five samples were prepared from  $X_p=0$  to  $X_p=0.90$ . AC samples were labeled as  $X_p=0$ ,  $X_p=0.16$ ,  $X_p=0.40$ ,  $X_p=0.70$ ,  $X_p=0.90$ , according to the respective phosphorus/precursor mass ratio used in the activation of each sample.

### **2.2 Textural characterization.**

Textural analysis of all samples was carried out by nitrogen adsorption/desorption at 77 K in an Autosorb-1 MP (Quantachrome, U.S.A.) volumetric adsorption apparatus. Specific surface areas were determined according to the BET method and the micropore volumes were estimated using the Dubinin-Radushkevich (DR) equation (Dubinin, 1967; Rouquerol et al., 2014). The micropore volume by the DR equation was also calculated using CO<sub>2</sub> adsorption isotherms at 300 K, as measured in the microcalorimetric system.

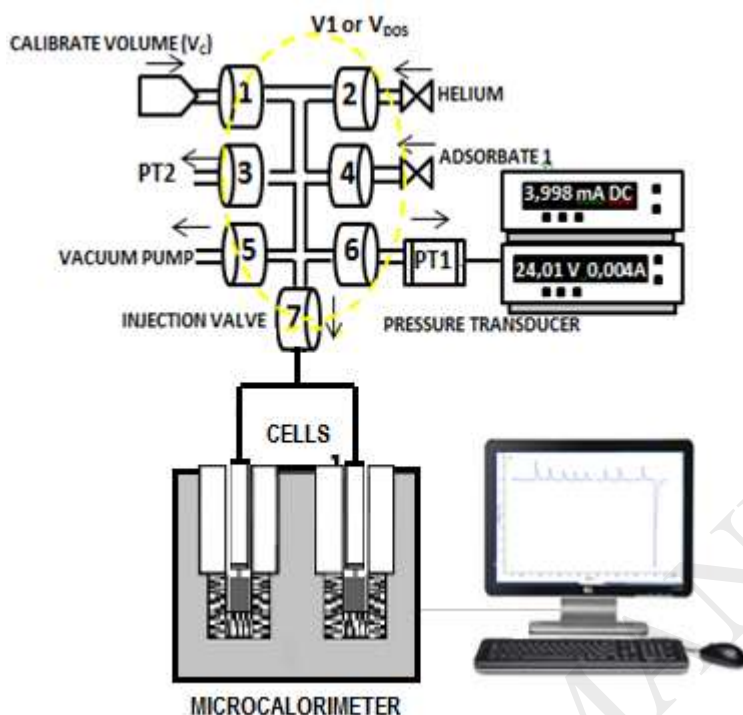
### **2.3 Temperature-Programmed Decomposition (TPD).**

The surface oxygen groups have an important role on the surface chemistry and adsorption behavior of activated carbons. These groups are usually placed on the edges of the basal planes of the carbon structure. These sites are associated with high concentrations of unpaired electrons and may play a significant role in oxygen chemisorption (Zawadzki, 1989). The activated carbon samples with different degrees of activation were subjected to heat treatment under helium flow (10 K.min<sup>-1</sup>), in order to decompose the oxidized functional groups formed by carbonization at ambient air until 1173 K. This analysis was carried out on CHEMBET 3000 (Quantachrome, U.S.A.) TPD apparatus. A Thermal Conductivity Detector (TCD) detected the gases released during heat treatment.

### **2.4 Adsorption Microcalorimetry.**

The activated carbon samples were also characterized using adsorption microcalorimetry, which provides a direct measurement of the adsorption enthalpy as a function of coverage. In order to simultaneously measure the adsorbed concentration and the respective heat released, a manometric setup was coupled to the microcalorimeter. The manometric setup was built in stainless steel with *Swagelok* VCR connections, as shown in Figure 1. The adsorption setup includes a vacuum pump (model E2M1.5; *Edwards*, UK), gas inlets, a pressure transducer (model 204; *Setra System*, Boxborough, MA) in the range from 10<sup>-5</sup> to 133 kPa, pneumatic diaphragm valves, a calibrated cylinder and two microcalorimetric cells. The sample cell is identical to the reference cell, as a “twin like” calorimeter (Calvet and Prat, 1963). The volume of each part of system was determined by gas expansion experiments using helium and a calibrated volume (10 cm<sup>3</sup>, *Swagelok*). This system is an improvement of

the system reported previously (da Silva et al., 2012), that was already tested with a reference material.



**Figure 1:** Manometric system of the adsorption microcalorimetric setup that mainly comprises pneumatic diaphragm valves (1-7) and two microcalorimetric cells (below valve 7).

Prior to each adsorption experiment, the samples were outgassed and heated up to 423 K for 12 h. The adsorption experiments were carried out at 300 K. The heat evolved during each adsorption step was measured using a Tian-Calvet microcalorimeter (model CA-100; ITI, Del Mar, CA) (da Silva et al., 2012). This apparatus comprises two identical calorimetric chambers inside an aluminum block to accommodate the reference and the adsorption cells. The aluminum block provides a large thermal sink for rapid heat dissipation and small temperature rise (less than 0.1 K). There are hundreds of thermopiles in the sample chamber connected in series to the thermopiles of the reference chamber with reversed polarity to reduce background noise. Each set of thermopiles was electrically calibrated by Joule effect, as described elsewhere (García-Cuello et al., 2009), in order to determine the calibration constant  $K$  of the equipment, which converts the areas of voltage peaks into thermal energy

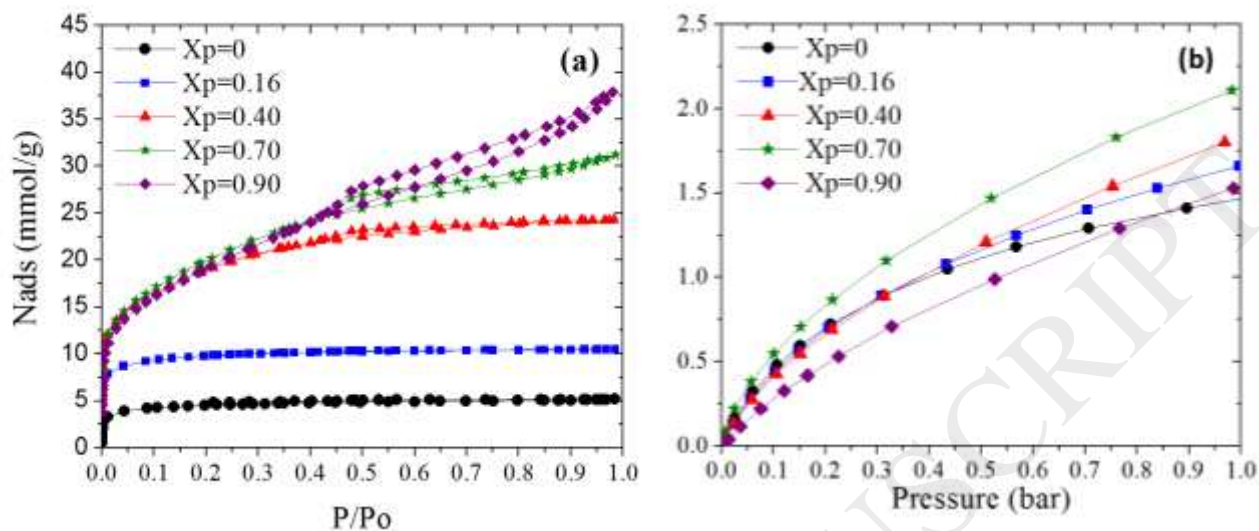


units. This microcalorimetric system has the sensitivity of  $0.15 \text{ V.W}^{-1}$  and the accuracy of each experimental point is  $\pm 7\%$ .

### 3. Results and Discussion

#### 3.1 $\text{N}_2$ and $\text{CO}_2$ adsorption isotherms

The adsorption-desorption isotherms of nitrogen at 77 K for the activated carbons synthesized from peach stones by chemical activation with  $\text{H}_3\text{PO}_4$  are shown in Figure 2 (a). Samples with different degrees of impregnation ( $X_p$ ) clearly show a different development of porosity. The presence of a "plateau" in the samples with low or no chemical activation ( $X_p=0$  and  $X_p=0.16$ ) indicates that mesopores are not developed. In such samples, the small interval of relative pressure required to achieve the "plateau" is an evidence of a narrow range of pore sizes. Molina-Sábio and co-workers (Molina-Sabio et al., 1995) observed, by SEM (Scanning Electronic Microscopy) images, the effects of depolymerization and re-polymerization of cellulose produced by phosphoric acid activation. They report that the morphology of carbons activated with low acid/precursor ratio was almost identical to that of the simply calcined sample with no chemical activation and increasing the concentrations of acid leads to a clearly etched surface. A similar effect is observed in Figure 2 (a). Even though the isotherms are parallel to each other for the two lowest activation degrees ( $X_p$ ), the other isotherms have quite different shapes. Those authors explain that, at higher concentrations of activating agent, the original cell morphology of the precursor is lost because most of the cellulose structure is degraded and extracted from the particle. This reorganization changes the initial characteristics of the precursor to produce a new porous structure, now including micro and mesopores. Samples  $X_p=0.40$ ,  $X_p=0.70$  and  $X_p=0.90$  showed H4 hysteresis which is typical of activated carbons and other materials having "slit" shaped pores or parallel plates. The fact that the sorbate evaporation responsible for the closure of the desorption branch occurs at relative pressures between 0.4 and 0.5 has been associated to a process of cavitation (Thommes et al., 2012). The presence of hysteresis is also clear evidence of the existence of mesopores (Rouquerol et al., 2014), which is consistent with the pore size distributions presented in Figure 3.



**Figure 2:** N<sub>2</sub> (a) and CO<sub>2</sub> (b) adsorption isotherms at 77 K and 300 K, respectively.

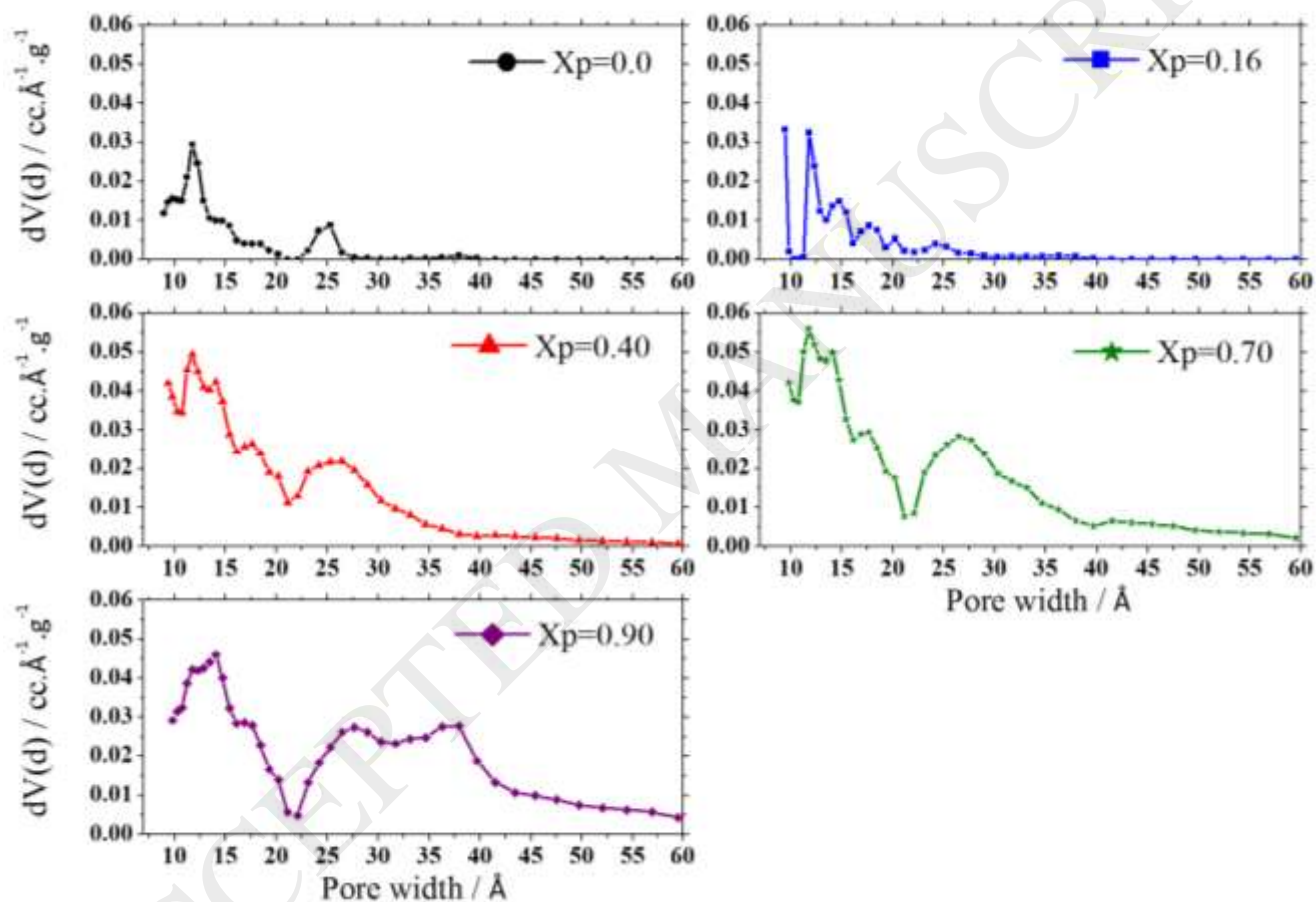
In figure 2(b), CO<sub>2</sub> adsorption isotherms at 300 K are observed, as measured in the microcalorimetric system. Sample X<sub>p</sub>=0.70 has the highest CO<sub>2</sub> uptake in the range of pressures under study, followed by samples X<sub>p</sub>=0.40 and X<sub>p</sub>=0.16. The uptake at 1 bar (between 1.5 and 2 mmol/g) is comparable to the values reported in the literature for low pressures (Hedin et al., 2010; Lozano-Castello et al., 2005; Toso et al., 2013). Low-pressure CO<sub>2</sub> isotherms are not a good parameter to study the storage capacity of the samples, since the isotherms are measured at a condition very far from the saturation pressure, similar to CO<sub>2</sub> isotherms at 273 K up to 1 bar. However, it is useful for the purpose of investigating the narrow micropore structure (below 9 Å) (Rouquerol et al., 2014). It is well known that N<sub>2</sub> at 77 K often does not access smaller pores due to diffusion restrictions, thus CO<sub>2</sub> isotherms with calorimetric tracking can be used to investigate this range of micropores. Based on a kernel of CO<sub>2</sub> isotherms at 300 K (Silvino et al., 2013), we calculated the pore fraction from 3 to 9 Å and present these along with other textural parameters in Table 1. We observed that, on average, the volume of micropores not accessed by N<sub>2</sub> is approximately 30% of the previously N<sub>2</sub> accessed micropore volume.

A significant increase in specific surface area ( $A_{\text{BET}}$ ) is observed for higher degrees of activation. Likewise, calculated micropore volumes from  $N_2$  isotherms (from 9 to 20 Å) also increase with activation, confirming the fact that, in the chemical activation with phosphoric acid, the porosity is closely related to the degree of impregnation (Molina-Sabio and Rodríguez-Reinoso, 2004). The specific surface area was determined by the BET method, which is also an important parameter for the characterization of porous materials, although the assumptions of the BET model do not strictly apply to the filling of micropores (Rouquerol et al., 2007). To reduce the error in these determinations, which are very susceptible to variations according to the pressure range considered for data regression, recommendations by Rouquerol et al. (Rouquerol et al., 2014) were followed. The total pore volume was calculated by the Gurvich rule. A characteristic feature of chemical activation is the maintenance of the volume of narrow micropores (as measured by  $N_2$  at 77 K) as the values of  $X_p$  increase (Molina-Sabio et al., 1995). Our samples reproduce this behavior presenting almost no changes in the amount of micropores (samples  $X_p = 0.40$  0.70 and 0.90), while the volume of mesopores increases significantly (Table 1 and Figure 3).

**Table 1:** Summary of the textural parameters for AC samples from peach stones by chemical activation with phosphoric acid.  $X_p$  indicates phosphorus/precursor mass ratios

Sample	$A_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{micro}}$ DR $N_2$ ( $\text{cm}^3/\text{g}$ ) (9 to 20 Å)	$V_{\text{micro}}$ GCMC $\text{CO}_2$ ( $\text{cm}^3/\text{g}$ ) (3 to 9 Å)	$V_{0.95}$ Gurvich ( $\text{cm}^3/\text{g}$ )
$X_p=0$	388	0.16	0.13	0.18
$X_p=0.16$	856	0.36	0.16	0.36
$X_p=0.40$	1744	0.56	0.19	0.84
$X_p=0.70$	1943	0.58	0.21	1.08
$X_p=0.90$	1922	0.55	0.16	1.31

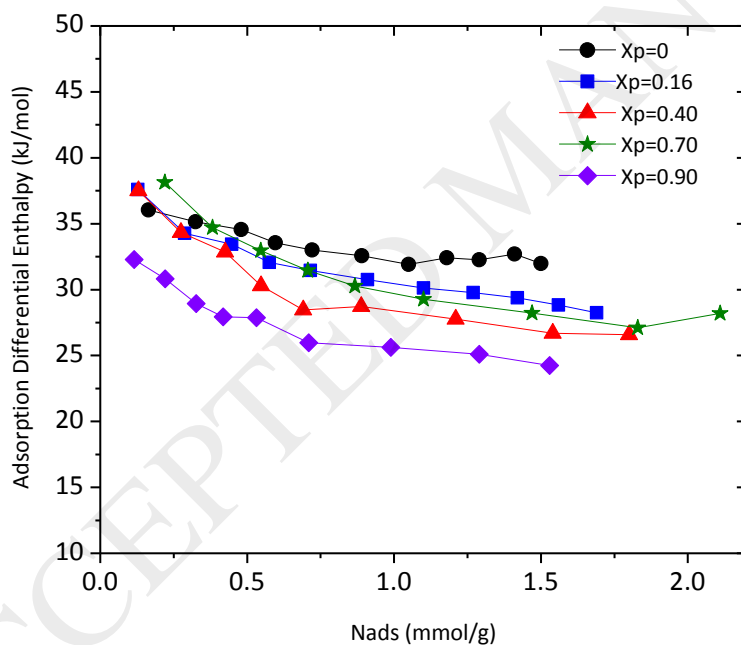
NLDFT model was used to calculate the Pore Size Distributions (PSD) for perfect slit pores between 5 to 60 Å. Figure 3 shows that the PSDs reflect the large differences in porosity of the samples. For the sample without chemical activation ( $X_p=0$ ), the micropores are formed only by the pyrolysis of lignocellulosic structure. For more activated samples, a wider pore size distribution is observed, and the amount of pores greater than 2 nm increases proportionally to the degree of impregnation. This was also evidenced by the presence of hysteresis type H4 in the isotherms, as discussed above.



**Figure 3:** Pore Size Distribution calculated from  $N_2$  isotherms at 77 K of the AC samples using slit model NLDFT

### 3.2 Microcalorimetric measurements

In order to extract additional information about the micropore structure of the activated carbon samples, Figure 4 shows the curves of CO<sub>2</sub> adsorption enthalpy. Differential adsorption enthalpies vary from  $-38$  down to  $-24$  kJ.mol<sup>-1</sup> and become roughly constant at high loadings, particularly for the sample Xp=0. The behavior of the experimental curves suggests that the interaction of carbon dioxide with the AC surface at low loadings occurs in sites of higher energy (narrowest pores). The magnitude of this initial enthalpy is closely related to the volume of micropores with sizes below 20 Å, as observed in the micropore volumes on Table 1. These narrow micropores, which act as active sites that attract the gas molecules, are also the ones that prevent a sharper fall of the enthalpy curve. As loading increases, adsorption occurs on wider pores, which involve weaker interactions. This decreasing behavior is frequently observed in heterogeneous adsorbents (Llewellyn, 2000).



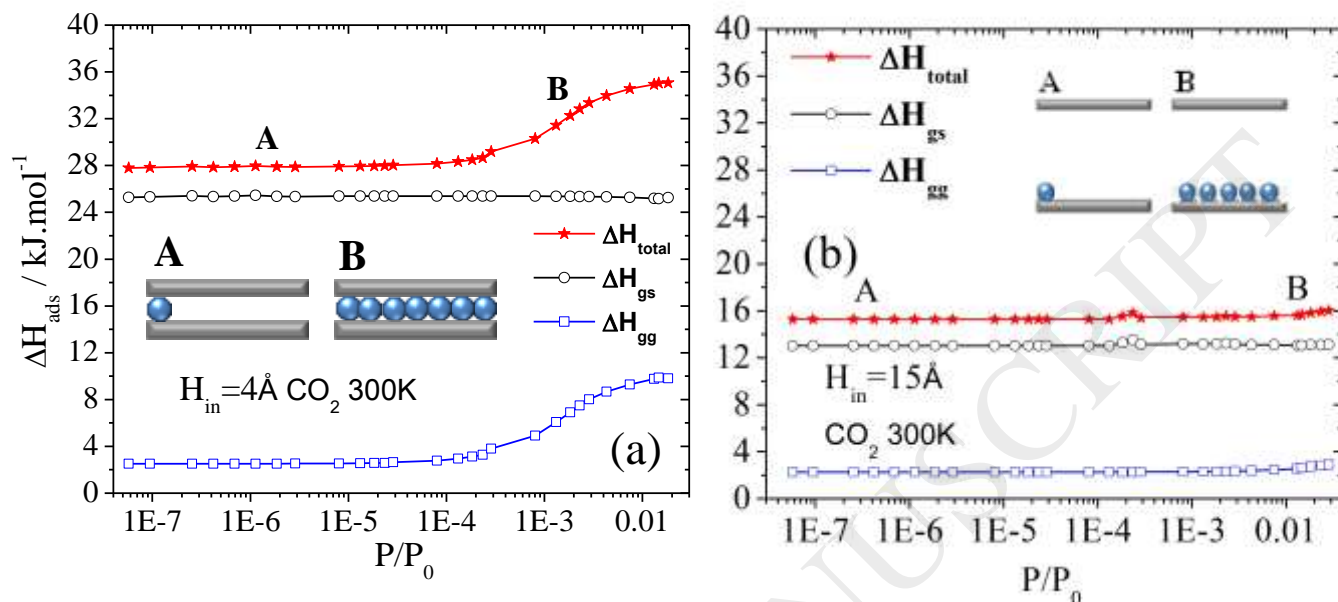
**Figure 4:** CO<sub>2</sub> adsorption enthalpies at 300 K for AC samples

Even though the sample with Xp=0 did not undergo chemical activation, its adsorption enthalpy did not match the one calculated by Bottani et al. (Bottani et al., 1994) for graphite samples. They state that the isosteric enthalpy of adsorption on graphitic surfaces varies from

-14 kJ/mol to -19 kJ/mol, depending on the degree of surface coverage. The mean adsorption enthalpy of -33 kJ/mol of the  $X_p=0$  sample confirms the small amount of micropores found in  $N_2$  PSD (Figure 3). Sample  $X_p=0.90$  has the lowest value of “zero coverage” enthalpy. This sample has a high total pore volume, but the  $N_2$  PSD shows a considerable fraction of larger pores with sizes from 20 to 40 Å (Figure 3). Hence, it is to be expected that the enthalpy curve had lower values than those of the other samples in the whole loading range under study.

The theoretically calculated energy contributions (Figure 5) help explain the decreasing enthalpy evolution of samples  $X_p=0.16$ ,  $X_p=0.40$  and  $X_p=0.90$  where two pore filling regimes are clearly discriminated (Figure 4). These theoretical calculations of adsorption heat are shown in two typical pores of the carbon series under study. We observed that the adsorption heat drops dramatically between the 4 Å and the 15 Å pore (from 28 to 16 kJ/mol). The pore filling regime at high energy correlates well with the microporous region, followed by an energy drop corresponding to the filling of the larger pores. Sample  $X_p=0$  has a flat enthalpy profile resulting from its narrow pore size distribution. Finally the sample  $X_p=0.90$  differs from the others by the low values of heat of adsorption indicating a very small volume of micropores ( $< 9$  Å) as a consequence of the high severity of  $H_3PO_4$  attack, at which condition the carbon microstructure begins to degrade. The adsorption enthalpy measurements clearly identify sample  $X_p=0.70$  as the most suitable for  $CO_2$  capture, which is readily confirmed by the  $CO_2$  isotherm obtained from the simultaneous microcalorimeter experiment (Figure 2b).

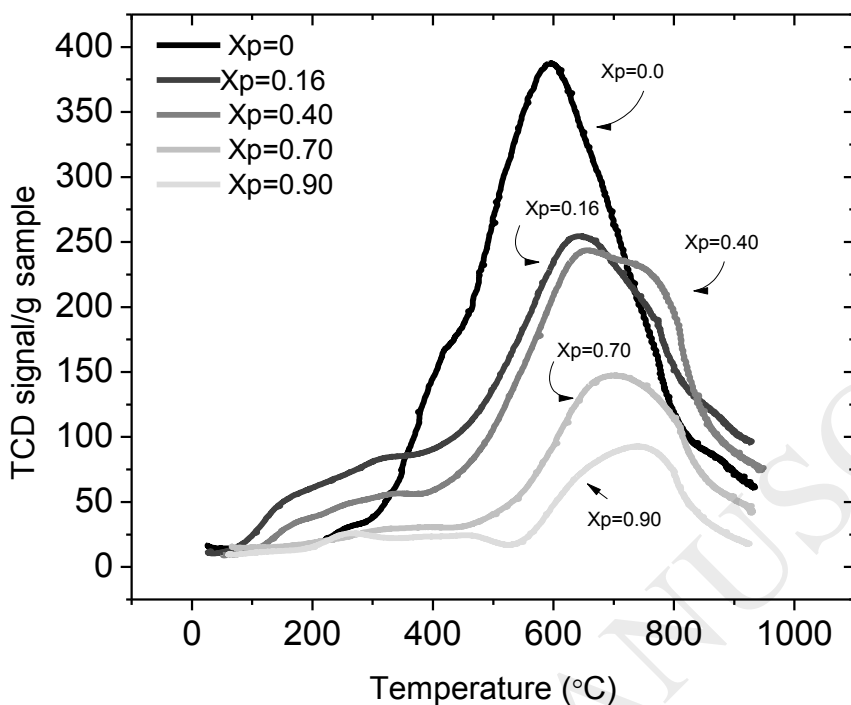
The results of Figure 5 was based in the carbon slit pore model and unit atom parameters. The interaction energy parameters between two  $CO_2$  molecules was calculated from the classical 12-6 Lennard-Jones potential equation (Alexandre de Oliveira et al., 2011). The interaction energy between a fluid particle and a single pore wall at a distance  $z$  (measured between the centers of the fluid atom and the atoms in the outer layer of the solid) was described by the Steele's 10-4-3 potential (Steele, 1974). Due to the small pores, adsorption of  $CO_2$  using the slit pore model was investigated by biased Grand Canonical Monte Carlo simulations (Lucena et al., 2008). The following values for the molecular parameters were used:  $\sigma = 3.65$  Å and  $\varepsilon/k = 246.15$  K (Alexandre de Oliveira et al., 2013).



**Figure 5:** Theoretical calculation of adsorption enthalpy in two typical pores of the carbon series studied (a) 4 Å and (b) 15 Å. For the smaller pore the main energy comes from the gas-solid interaction at low pressures; close to pore filling, a substantial contribution also comes from the fluid-fluid interaction. In the larger pore, gas-solid interaction predominates at all pressure range.

### 3.3 Temperature-Programmed Decomposition (TPD).

The surface chemistry of activated carbons was essentially determined by the amount of oxygen surface complexes. Figure 6 shows the TCD signal per gram carbon of the effluent gas from our samples subjected to thermal decomposition under helium flow (TPD). The profiles are characterized by the evolution of decomposition gases: CO<sub>2</sub> at low temperatures and CO appearing at about 873 K. Samples with peaks shifted towards high temperatures (> 1073 K) suggest the presence of stable oxygen groups such as ethers, carbonyls or quinones (Belhachemi et al., 2014). The amount of oxygen as determined by this technique provides the bulk content, unlike other techniques, such as XPS (X-ray Photoelectron Spectroscopy), which determines only the surface concentration (Figueiredo et al., 1999).



**Figure 6:** Temperature-Programmed Decomposition results

TCD detection does not distinguish between CO and CO<sub>2</sub>, but it can be used as a comparative tool to illustrate the differences of total gases evolved upon thermal decomposition of each sample. The results show that the highest amount of decomposition gases evolve from sample X<sub>p</sub>=0. Generally speaking, the amount of evolved gas upon thermal decomposition is inversely proportional to the degree of impregnation, that is, less activated samples possess more oxygen functional groups (Molina-Sabio et al., 1995). Furthermore, the decomposition temperature increases continuously for more activated samples. This may be evidence that most oxygen groups are originally due to the chemical composition of the precursor itself and its carbonization. The activation with H<sub>3</sub>PO<sub>4</sub> tends to remove those oxygen groups, which are less thermally stable, and the final AC tends to have a more apolar and hydrophobic surface.

TPD is a reliable technique to assess the oxygen content of a carbon sample. Basai et al. (Bansal et al., 1977) verified that the amount of oxygen evolved as function of the heat



treatment temperature agrees well with the total oxygen obtained by ultimate analysis. The surface groups from which CO<sub>2</sub> evolve are less stable and begin to decompose at 350 °C whereas CO evolves only above 773 K. Figueiredo et al. (Figueiredo et al., 1999) also studied the surface chemistry of oxidized activated carbons using Temperature-Programmed Desorption coupled to a mass spectrometer to discriminate between CO and CO<sub>2</sub> released upon the thermal decomposition of each sample. They show a gradual increase in CO and CO<sub>2</sub> released as the degree of oxidation of samples increases. Similarly, a gradual behavior is observed in Figure 6, with the signal decreasing for higher degrees of chemical activation. It seems that the increase of phosphorus concentration largely prevents the creation of oxygenated groups on the surface.

Although the chemical characteristics of the surface of the samples is expected to be a relevant issue in the discussion of the adsorption enthalpy results, no particular correlation associated with surface oxygen concentration was observed in the enthalpy values calculated with the microcalorimeter. In particular, we observed that although sample X<sub>p</sub>=0.40 presented higher oxygen percentage than sample X<sub>p</sub>=0.70, it resulted in lower CO<sub>2</sub> adsorption performance.

#### 4. Conclusions

A set of AC samples from peach stones was prepared by chemical activation with H<sub>3</sub>PO<sub>4</sub> and characterized by N<sub>2</sub> and CO<sub>2</sub> isotherms at 77 K and 300 K, respectively. Differential CO<sub>2</sub> adsorption enthalpic curves as a function of loading were measured by microcalorimetry, in order to investigate the pore filling regimes in the carbonaceous material. By means of temperature-programmed decomposition (TPD) experiments under inert atmosphere, it was also possible to rule out the influence of surface oxygen groups on CO<sub>2</sub> adsorption.

It was found that a higher phosphorus/precursor impregnation ratio (X<sub>p</sub>) leads to an increasing fraction of micropores and mesopores, and the micropore volume (below to 20 Å) is maximal at X<sub>p</sub>=0.70. Higher X<sub>p</sub> also leads to adsorbents with a lower density of oxygenated functional groups. In the samples with pores in the micropore and mesopore range, the adsorption enthalpy profile progressively decrease giving rise to two different pore

filling regimes. In the samples where the pore size distribution was narrower, the enthalpy profile became more flat. We have not noticed any interference in the enthalpy profiles that can be attributed to oxygen surface groups. For the series of activated carbons under study, adsorption microcalorimetry were well correlated with the pore size distribution, allowing for a clear screening between samples aimed at CO<sub>2</sub> adsorption. A theoretical validation of the pore filling regime was obtained through molecular simulation calculations where the solid-fluid and fluid-fluid interaction energy were discriminated for typical pore sizes found in the activated carbon samples.

This study confirms that CO<sub>2</sub> microcalorimetry measurements in this series of carbons coupled to Monte Carlo simulations allowed discriminating between micropore and macropore filling regimes. By comparison of the density of surface oxygen group with differential enthalpy data, we ruled out that surface chemistry heterogeneities play a significant role in the adsorption enthalpy of CO<sub>2</sub>.

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