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Thermodynamic of the Interactions Between Gas-Solid and Solid-Liquid on Carbonaceous Materials

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1. Introduction

For decades the man has had to face one of the major problems resulting from technological development and global population growth, environmental pollution, which has impacted on the different systems of life. The impacts of technological progress attained by man, have necessitated the establishment of international rules and regulations that set limits and establish a balance between development and the effects caused by the same (**Rodríguez 2003, Callister 2007, Rodriguez-Reinoso, 2007**). For this reason, we have launched various alternative solutions to environmental problems, including the synthesis and use of porous materials from organic waste or waste products with high carbon content, has been successful mainly in catalysis, adsorption and gas separation.

Activated carbon is a material that consists of microcrystals elementary hexagonal planes which are not well targeted, but displaced relative to each other and overlapping each other, so they have a high percentage of highly disordered structure. In fact there are hexagonal folding sheets with spaces of varying size (usually less than 2 nm) which make up the porosity of the material (**Marsh & Rodriguez-Reinoso, 2006**). These characteristics confer an exceptionally high surface area and good absorbent properties can be exploited in different areas. The production of activated carbon is linked to the purification of products and environmental protection. To the extent that the demands of purity of products require more sophisticated processes and emissions standards become more stringent, the activated carbon evolves, the production of the classic styles granular and powder have been joined by other like fibers, fabrics, monoliths among others (**Blanco et al., 2000**). Forms of activated carbon that are known and marketed, recent studies have shown that the monoliths exhibit characteristics that differentiate them from conventional ways, including the following highlights: allow the passage of gases with a very drop small, have a high geometric surface per unit weight / volume, the gas flow is very uniform, with easy handling, resistance to friction, reduce the constraints generated by phenomena of internal diffusion and mass transfer, these properties the have become used as support materials or adsorbents that favor direct adsorption process in the gas phase (**Nakagawa et al., 2007**).

In addition to their interesting adsorptive properties, during the process of obtaining activated carbons it is possible to modify and / or design their properties through a treatment of pre-or post-synthesis in order to obtain materials. These materials can be intended for more specific uses taking into consideration that the adsorption capacity of activated carbon depends on its textural characteristics and also on its surface chemistry (**Dias** *et al*. **2007, Petit et al. 2010**). The surface chemistry of activated carbon is determined by the presence of atoms different from carbon atoms in graphene layers also known as heteroatoms, the most common are: oxygen, hydrogen and nitrogen. These heteroatoms produce a wide variety of surface groups, these groups can be acidic such as: carboxylic, lactone, anhydride and phenolic, while the basic character is attributed to groups such as quinones, pyrones besides of the delocalized π electrons in graphene layers or with a neutral character like carbonyl and ether (**Montes-Moran** *et al*. **2004,Rivera-Utrilla & Sanchez-Polo. 2003**); surface groups determine parameters such as acidity and total basicity, surface charge and hydrophobicity, this will depend mainly on the type and concentration of groups on the surface of activated carbon.

Surface chemistry of activated carbon can be modified mainly by oxidation treatments and controlled thermal treatments that promote the formation and / or selective removal of different groups, as reported by Figueiredo and Pereira 2010. The role of surface chemistry in adsorption of gases, metal ions and organic molecules, is mainly due to specific interactions between surface groups and the different species.

In general, any organic material with relatively high carbon content is capable of being transformed into activated carbon. The activated carbon produced by manufacturing can come from wood and forest residues or other biomass (peat, lignite and other coals) as well as various polymers and natural or synthetic fibers. The factors that must be taken into account when choosing a suitable precursor are good availability and low cost, low mineral content and the resulting carbon possesses good mechanical properties and adsorption capacity. Wood waste, coconut shells, nuts, seeds and fruits along with some coals and petroleum coke are the most commonly used precursors (**Giraldo et al. 2008**). The complexity of the structure of activated carbon, can be characterized textural, chemical and energy by using different techniques among which include: physical adsorption of gases or vapors, scanning electron microscopy (SEM), electron microscopy transmission (TEM), infrared spectroscopy (FT-IR), X-ray diffraction, temperature programmed desorption (TPD), mercury porosimetry, immersion calorimetry and adsorption rates of methylene blue adsorption, density, size, moisture , ash, abrasion resistance and other parameters applicable to the specifications of coal (**Marsh & Rodriguez-Reinoso, 2006**).

The most common use is given to activated carbon adsorption processes of pollutants in liquid and gas phase. Adsorption is a process by which atoms, ions or molecules are trapped or retained on the surface of a material, which is different from absorption, which involves volume. This process involves an adsorbent, which in this case is activated carbon and adsorbate, which is the contaminant retained

The adsorption is exothermic, which can be classified as chemical or physical, depending on the magnitude of the interactions established between the retained material and the adsorbent surface. The amount of material that accumulates depends on the dynamic equilibrium is reached between the rate at which the material is adsorbed to the surface and the speed at which it evaporates or releases, in turn, they usually depend importantly on temperature.

Adsorption is a simple and attractive method for removing contaminants in aqueous phase, due to its high efficiency and easy handling. Given that the adsorption phenomenon is clearly exothermic, it is possible to characterize all the interactions inherent in the process of adsorption. For this purpose we describe the phenomenon of adsorption in terms of energy:
If the interaction is solid-gas, may be the differential molar enthalpy of adsorption from the molar internal energy of the adsorbed phase and energy Ua adsorbate molar Ug, then, the change in internal energy as a result of adsorption can be represented as:

$$\frac{\Delta U_a}{n_a} = \overline{U}_a - \overline{U}_g = \Delta\overline{U}_a \tag{1}$$

In which, $\frac{\Delta U_a}{n_a}$ = is the molar energy change of the system, caused by the transfer of n moles of adsorbate from the gas phase to the adsorbed state.
This change in molar internal energy of the system is the integral molar energy of adsorption, ΔUa, which depends on interactions adsorbate-adsorbate and adsorbate-adsorbent. Ua is the average molar internal energy, for all the adsorbed molecules.
When an infinitesimal amount of moles of adsorbate, dna, is transferred to the solid surface from the gas phase at constant volume, the change in internal energy of the system will:

$$\overline{\Delta U_a} = \overline{U_a} - \overline{U_g} \tag{2}$$

Where $\Delta\overline{U_a}$ = is the differential molar energy of adsorption, and is defined as:

$$\overline{U_a} = \left(\frac{\partial U_a}{\partial n_a}\right)_{T,A} \tag{3}$$

Similar to what was expressed for energy,

$$\Delta H_a = H_a - H_g \tag{4}$$

Where Ha and Hg are the molar enthalpies of the adsorbate adsorbed state and gas phase. Likewise, the differential molar adsorption enthalpy is:

$$\Delta\overline{H_a} = \overline{H_a} - \overline{H}_g \tag{5}$$

In which:

$$\overline{H_a} = \left(\frac{\partial H_a}{\partial n_a}\right)_{T,P} \tag{6}$$

With the theoretical basis described above, it is possible to know then the extent of heat evolved in the adsorption process, known as heat of adsorption and is defined as a thermodynamic function, which can be used to characterize the surface of a solid .
There are two ways of expressing the heat of adsorption:

Integral heat of adsorption, amount of heat, Q, released when one gram of solid adsorbent adsorbs x grams. Its units are Joules / gram of adsorbent.
Differential heat of adsorption, ΔH, amount of heat generated when x moles of adsorbate adsorbed. Its units are Joules / mole of adsorbate.
The differential heat of adsorption is also known as isosteric heat of adsorption and can be determined by using calorimetry or by adsorption isotherms, measured at two or more temperatures. (**Bansal et al. 1988, Moreno-Piraján & Giraldo, 2007**).
On the other hand, it is necessary to know the pore structure of the solid. Thus, for microporous solids without external surface (**Kraus 1955**), ΔHi immersion enthalpy is related to the isosteric heat of adsorption q^{isost} by the expression:

$$-\Delta H_i(T) = \int_0^1 q^{isost.}(T;\Theta)d\Theta - \Delta H_{vap.}(T) \tag{7}$$

Where:

Θ= degree of volume filling W/Wo

The negative sign is because q^{isost} convention is positive, while ΔHi is negative.
Dubinin **(Moreno-Piraján & Giraldo 2007, Dubinin 1975)** define of net Heat of adsorption (q^{net}) as:

$$q^{net} = q^{isost.} - \Delta H_{vap.}$$

when ΔH_{vap} is vaporization enthalpy.
For the general case of n, the above equation becomes:

$$q^{net} = E_0\left[\left(\ln\frac{n_a^o}{n_a}\right)^{\frac{1}{n}} + \left(\frac{\alpha T}{n}\right)\left(\ln\frac{n_a^o}{n_a}\right)^{\left(\frac{1}{n}\right)-1}\right] \tag{8}$$

Donde,
α = Thermal expansion coefficient of adsorbate
n_a = Amount adsorbed at relative pressure P/Po
n_a = Amount adsorbed ar relative pressure P/Po
Eo= Characteristic energy for vapor adsorption
Θ = Micropore filling degree
For activated carbons with n=2

$$q^{net} = \beta E_o[\left(\ln\frac{1}{\Theta}\right)^{\frac{1}{2}} + \left(\frac{\alpha T}{2}\right)\left(\ln\frac{1}{\Theta}\right)^{-\left(\frac{1}{2}\right)}] \tag{9}$$

$$-\Delta H_i = \int_0^1 q^{net} d\Theta$$

By replacing in equation (9):

$$-\Delta H_i = \beta E_o \int_0^1 \left(\ln\frac{1}{\Theta}\right)^{\frac{1}{2}} d\Theta + \frac{\alpha T \beta E_0}{2}\int_0^1 \left(\ln\frac{1}{\Theta}\right)^{-\frac{1}{2}} d\Theta \tag{10}$$

The solution for the integrals of this type, is a function gamma (Γ(x))

$$\int_0^1 \ln\left(\frac{1}{x}\right)^p dx = \Gamma(p+1) \tag{11}$$

$$\Gamma(p+1) = \begin{cases} para\, p = \frac{1}{2} : \Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2} \\ para\, p = -\frac{1}{2} : \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \end{cases} \tag{12}$$

Thus, equation (10) can be written as:

$$\Delta H_i = -\frac{\beta E_o \sqrt{\pi}(1+\alpha T)}{2} \tag{13}$$

Which is valid for the micropores filling, in activated carbons at temperature T (**Moreno-Piraján & Giraldo 2007**).
For a coal with a micropore volume W_o and an adsorbate with a molar volume V_m, Stoeckli and colleagues established a relationship between the enthalpy of different types of activated carbons in various body fluids and the parameters obtained by adsorption of vapors of these liquids on the same solid. In the equation of Stoeckli and Krahenbüehl (**Moreno-Piraján & Giraldo 2007, Stoekli & Kraehenbuehl 1989**):

$$\Delta H_i = -\frac{\beta E_o W_o \sqrt{\pi}(1+\alpha T)}{2V_m} \tag{14}$$

Which corresponds to the immersion enthalpy ΔH_i , en J/g.
Where β is the adsorbate affinity coefficient, E0 is the characteristic free energy of adsorption of vapor of reference, W_0 is the total volume of micropores of the solid, is the coefficient of thermal expansion at temperature T, and Vm is the volume molar.
The immersion in a nonpolar solvent, which is known molecular dimensions, and generate a thermal effect only by filling the micropores of the solid, relates the thermal effect of the adsorbent surface as follows

$$\Delta H_{\exp.} = \Delta H_i + h_i S_{ext.} \tag{15}$$

where h_i is specific enthalpy in J/m^2.
As the external surface is defined as:

$$S_{ext.} = \frac{\Delta H_{i\exp}}{h_i} - \frac{\Delta H_i}{h_i} \tag{16}$$

So, the external surface may be known as:

$$S_{ext.} = A_{TOTAL} - A_{MICROPO.} \tag{17}$$

For a solid contribution also presents the mesopores and macropores, the total area is expressed as:

$$A_{TOTAL} = A_{MICROP.} + A_{MESOP.} + A_{MACROP.} + S_{abierta.} \tag{18}$$

Where,
A_{TOTAL}: Total area
A_{MICROP}: Microporous area
A_{MESOP}: Mesoporous area
A_{MACROP}: Macroporous area
$S_{ABIERTA}$: Open area non-poorus
When activated carbon presents neither external surface nor development of meso and macropores, the experimental enthalpy will:

$$\Delta H_{\exp} = \Delta H_i \tag{19}$$

determinate by equation (15).
Until here, have been described the theoretical foundations of solid-gas interactions and solid-liquid, which can calculate the magnitude of the thermal effect generated and the type of interaction between the adsorbate and the adsorbent, which is proportional to the affinity between them, and allows for relationships that give an approximation of the surface area of adsorbent.
Now, referring to such calorimetric techniques, such as immersion calorimetry and adsorption for measuring the thermal effect of the interaction of a solid with a liquid or gas, which leads to determine the thermodynamic variables in different interfaces: solid-liquid, solid-gas and liquid-liquid, which provide valuable information about the behavior of the solid. Such is the importance of these techniques, which in recent years, several studies are focused on the design, construction and development of immersion calorimeters adsorption.

Calorimetric technique

Calorimetry is a technique used to measure a large number of processes that generate heat in their development, and which can determine the enthalpy changes DH and combination with other techniques to obtain the free energy change ΔG and entropy changes ΔS. Furthermore, this technique has been used to study physical and chemical events that occur on the surface of a solid. (**Moreno 1996**).
However, there is a team that is capable of performing all the above measures at a time, so different equipment should be used according to the type of study that you want to perform and the amount of heat generated in the system. For this reason, there are combustion calorimeters, adsorption and immersion, which basically consist of:
Calorimetric cell, which should be designed with a capacity that is associated with the type of sensors require the calorimeter and additionally must have regard to the material of construction depending on the system to be studied. In this cell are often attached a heating sample holder.
Electrical calibration system, which consists of an electrical circuit which provides power to the calorimeter to determine the constant of the system under study. Electrical work

supplied can be calculated if one knows the potential (Eh) through the heating resistor (Rh), the current (I) and heating time (t).

$$W_{elect} = Eh * I * t \tag{20}$$

Thermometric system for measuring thermal effect, which consists of different types of sensors, which can be proportional to the temperature or property connected with the transfer of heat.
According to the system you want to measure, you must use a specific calorimetric system. Below is a brief description of immersion calorimetry and sorption

Immersion calorimetry, measurement of solid-liquid interactions.

For many years, immersion microcalorimetry has been a useful technique for the characterization of powders and porous solids like activated carbons and oxides (Hemminger & Höhne 1984). Technique involves immersing a known quantity of a solid in a specific liquid, and measure the heat generated due to wet the solid, liquid immersion.
In the absence of complex effects such as filling of micropores, is usually taken as a first approximation, the energy due to the immersion of a solid degassed $\Delta_{im}U^o$, which is proportional to the solid surface, A, according to Equation 21:

$$\Delta_{im}U^o = A.\Delta_{im}u^{i,o} \tag{21}$$

in which the energy of immersion per unit area, $\Delta_{im}u^{i,o}$ is characteristic of the nature of solid-liquid system.
When $\Delta_{im}U$, is known for a given solid-liquid system, the adsorbent surface (A) can be evaluated. When the surface of the sample of adsorbent is less than 1 m^2, generates heat due to immersion, which is easily measured by colorimetric procedures and therefore the immersion microcalorimetry can be used to evaluate the specific surface of adsorbent (**Rouquerol et al. 1999**).
Immersion calorimetry is a useful technique to assess the total area and size distribution of micropores of a microporous carbon (**Denoyel et al.1993**), assuming that the energy of the dip is proportional to the area available for liquid immersion to any size and shape of the pores. In addition, it is assumed, from the point of view of energy per unit external surface area of solid has the same behavior (**Rouquerol et al. 1999, Hemminger & Höhne 1984**).
The Figure 1 shows the immersion calorimetric heat conduction unit. To experimentally measure the immersion heat, the adsorbent is immersed in the liquid which is to determine the interaction. You can use a microcalorimeter heat conduction, which is expected to be reached thermal equilibrium between all components of the calorimetric system: the cell containing the immersion liquid, the vial containing the solid under study, a heating pad for perform system calibration, temperature sensors should be arranged around the cell containing the immersion fluid and the surroundings. To achieve this, the entire system must be completely insulated from temperature fluctuations. Once thermal equilibrium is reached, it is the breaking of the ampoule to allow liquid to come into contact and the adsorbent, it ends with an electrical calibration. Throughout the experiment, recorded the potential generated by the sensors, should have the thermal effect sensor thermocouples or thermopiles and evaluates the area under the curve of the signal generated in response to solid-liquid interaction.

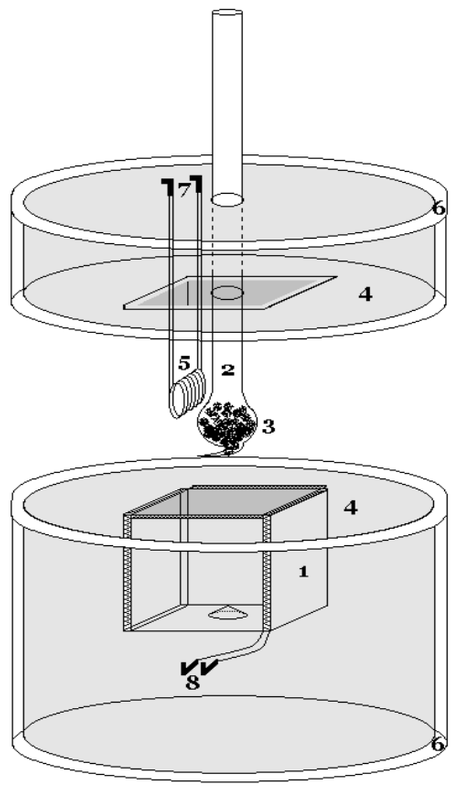


Fig. 1. Calorimeter immersion scheme Tian type. (1)Sensors System; (2) Sample cell; (3) Sample; (4) Heat Sink; (5) Heat resistance for calibration; (6) Insulation jacket; (7) Output of resistance to power supply; (8) Output of sensors system to interface multimeter.

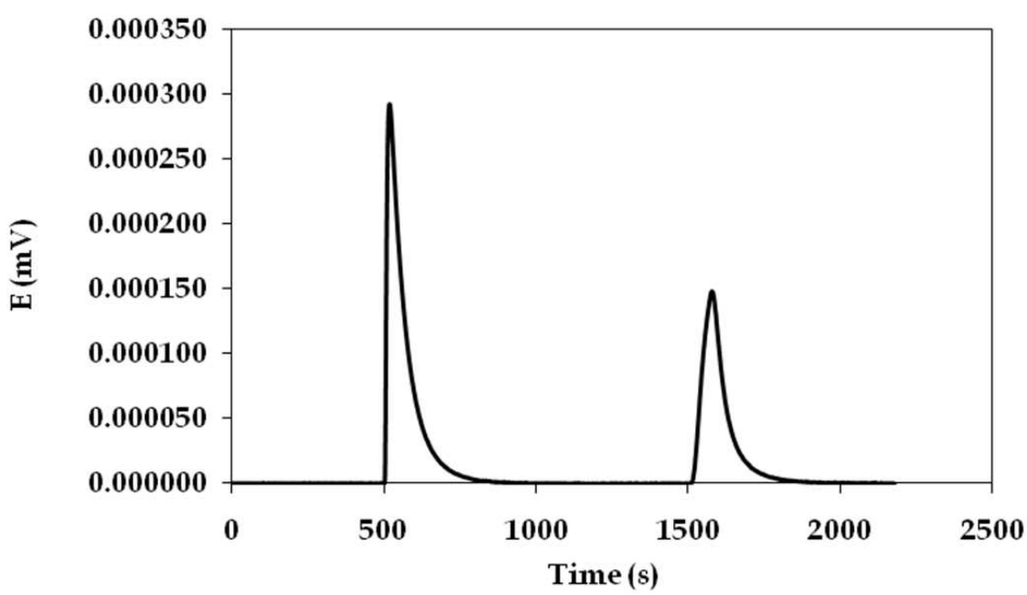


Fig. 2. Thermogram obtained for the immersion of an activated carbon pellet ore (CAP), in benzene

Figure 2 shows a typical thermogram obtained for the immersion of an activated carbon pellet ore (CAP), in benzene. It can be seen in the range of 0 to 500 seconds, the baseline obtained, which illustrates the heat balance and low noise level in the calorimetric signal. Table 1 shows the values of surface properties obtained by immersion calorimetry, for this same sample, two samples obtained by the modification of the CAP.

Sample	E_o kJ/mol	W_o cm^3/g	S_{BET} m^2/g
CAP	7.47	0.43	1248
CAPRED	6.48	0.38	1089
CAPN65	7.47	0.43	1253

Table 1. Surface properties obtained for three activated carbons by gas adsorption

The sample CAPRED is a modification of CAP, obtained by heating the same until 1373 K, under nitrogen, for 3h. CAPN65 sample is a sample obtained by modification of CAP through the impregnation of CAP with 65% HNO_3 and heating it to 473 K, for 2 hours.
As shown in Table 1, the modification with HNO3 and 65% did not produce a significant change in the surface properties of the sample. This behavior is attributed to the low temperature at which it made the change, which did not affect the porous structure of the solid. The modification to 1373K nitrogen affected the pore structure of the solid, reducing the volume of micropores and consequently, the surface area there of in Figure 3 shows the isotherms of nitrogen at 77 K for these three samples.

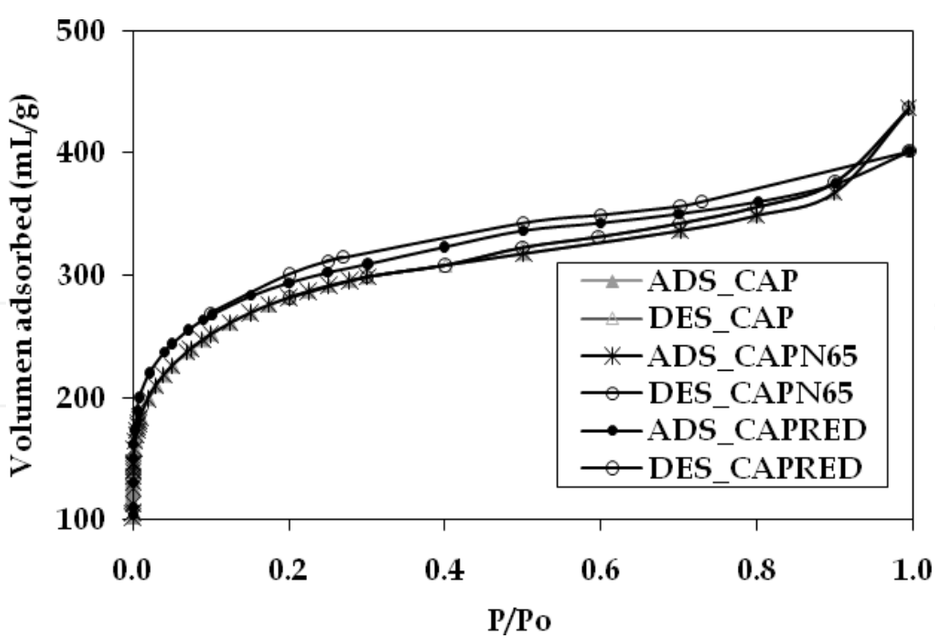


Fig. 3. Nitrogen adsorption isotherms at 77 K, for the three carbons under study

The isotherm can be observed further that the sample has CAPRED mesoporosity development, so it appears the hysteresis loop in it. CAP and CAPN65 isotherms are

virtually identical, confirming that the modification with 65% HNO_3 shows no effect on the texture of activated carbon.
Table 2 shows the surface properties obtained by immersion calorimetry for these three samples

Sample	S_{ext} m²/g	ΔH_{imm} J/g	ΔH_{exp} J/g	A_{MICROP} m²/g	A_{total} m²/g
CAP	37	-44	-48	1219	1256
CAPRED	55	-33	-39	1065	1120
CAPN65	64	-34	-41	1219	1283

Table 2. Surface properties obtained for three activated carbons by immersion calorimetry in benzene

The results for ΔH_{inm}, from equation (14). and ΔHexp are the experimental results. The external surface area Sext , of micropores $A_{MICROP,}$ and the total area A_{total}, were obtained from the equations (16), (17) and (18) respectively.
Table 3 shows the parameters used for calculations of surface properties obtained by immersion calorimetry into benzene.

α	B	Vm
1,24E-03	1	88,9

Table 3. Physical characteristics of benzene.

Figure 4 shows a relationship between the areas obtained by gas adsorption and that obtained by immersion calorimetry.

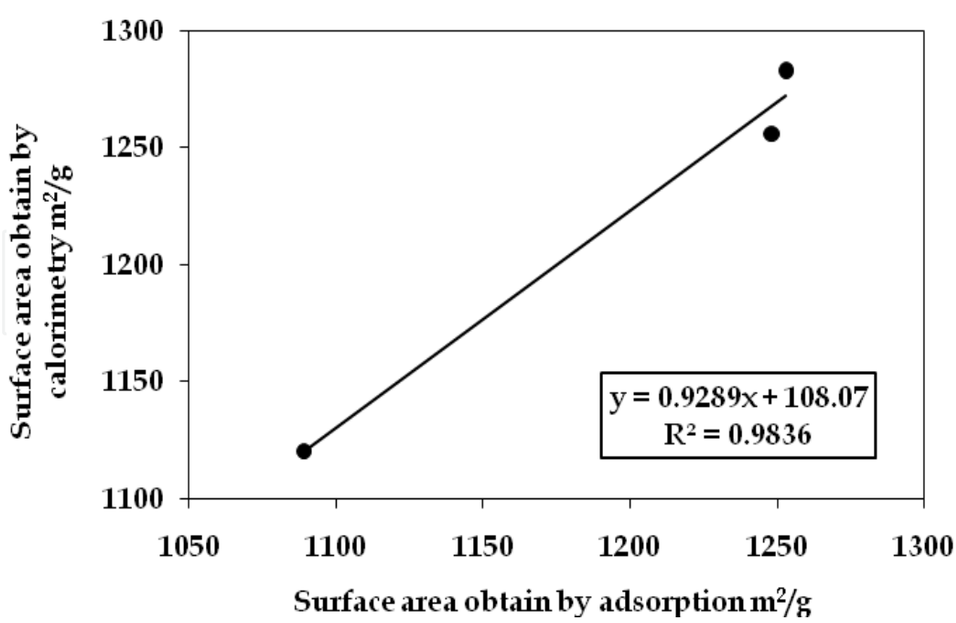


Fig. 4. Relationship between the total area obtained by adsorption calorimetry and nitrogen adsorption.

From these results we can see good correlation between the results obtained by the two methods compared, which shows a correlation coefficient of 0.9836, confirming that immersion calorimetry is a characterization parameter for solid-liquid interactions. You could make a more exhaustive with probe molecules of different sizes to benzene, since the pore size distribution can affect the calorimetric data (**Molina-Sabio et al. 2008**).

Adsorption calorimetry, measurement of solid-gas interactions.

There are several reasons to determine the heat of adsorption to characterize the surface energy of materials (**Rouquerol et al. 1999**), provide basic data for development of new theories of equilibrium and kinetics of adsorption (**Zimmermann & Keller 2003**), design and plants improve separation processes by adsorption and desorption, PSA, VSA, TSA and their combinations (**Ruthven 1984, Yang 1997**).
Adsorption calorimetry in combination with other physical or chemical properties to describe the properties of a solid surface (**Garcia-Cuello et al. 2009, Llewellyn & Maurin 2005, Garcia-Cuello et al. 2008, Moreno & Giraldo 2005**).
To experimentally measure the heat of adsorption, calorimetric unit is used as shown in Figure 5.

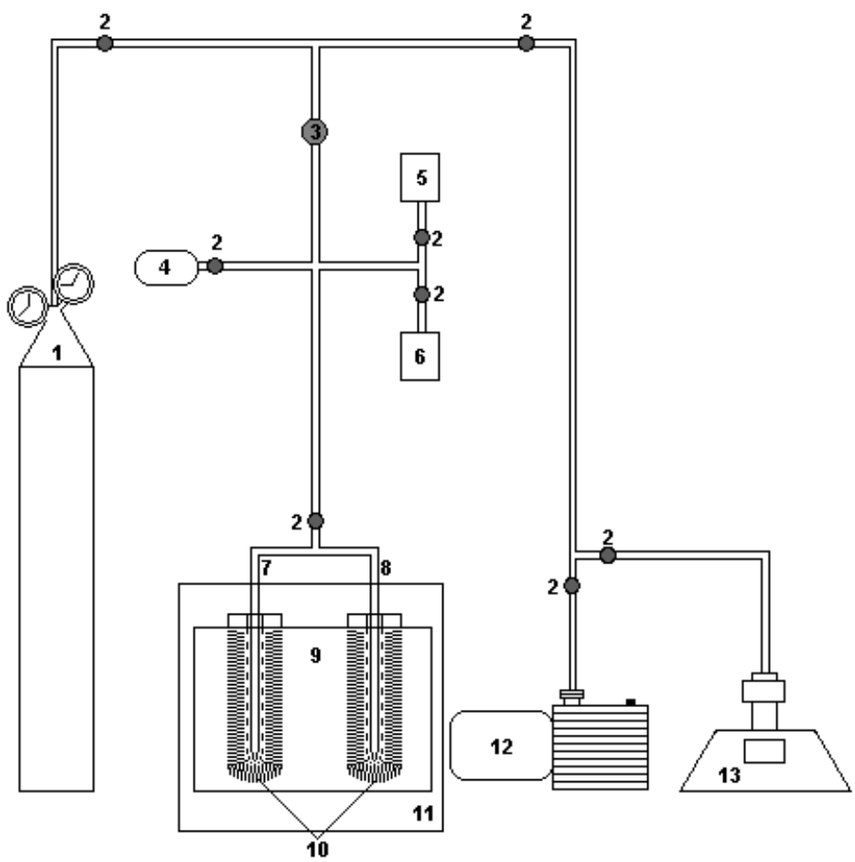


Fig. 5. Adsorption calorimeter scheme. (1) Adsorbate, (2) precision valves, (3) needle valve, (4) Volume calibration, (5) pressure transducer 1 to 1000mbar, (6) pressure transducer 10-4 to 1 mbar , (7) measuring cell, (8) reference cell, (9) Calorimeter adsorption (10) thermopile sensors in 3D layout type, (11) thermostat, (12) Rotary Vacuum Pump, (13) Pump ultra high vacuum

The heats of adsorption measured at a temperature of liquefaction of the adsorbate, in the case of nitrogen at 77 K and 273 K. CO_2 For this, use a thermostat bath at that temperature. Make contact with the solid adsorbate successive small doses. This allows measure the evolution of the interaction energy compared to coverage. Before start the calorimetric measurements. To start the measurements in the microcalorimeter, initially must be empty throughout the adsorption system, including the solid sample under study, using a vacuum system that achieves at least 10^{-3} Torr. When the system reaches the expected vacuum level, are the respective gas injection, waiting time for a balance between system components and are simultaneously recorded volumes of gas adsorbed and the heat evolved at each injection. Developed to sense heat, temperature sensors are used thermopile type, with appropriate sensitivity to detect heat from 10 to 100 J / g. Pressure readings are made using a pressure sensor with adequate sensitivity and precision must be known in the injection volume. The differential molar adsorption energy can be obtained by equation (3), and evaluating the area under the curve obtained in the experiment, which is the signal generated by the thermopile due to solid-gas interaction which is proportional to the adsorption energy (**Garcia-Cuello et al. 2008, Garcia-Cuello et al. 2009**).

Preparation, characterization, modification and use of carbonaceous Materials

Preparation, characterization, modification and use of carbonaceous materials like activated carbon in different presentation such as: granulate, powder, pelettes, char, monoliths, among other, it has been object investigation during many years. Next are presented some results of investigations developed in the by the authors about these porous solids and their employment in the adsorption of pollutants in liquid and gas phase.

Bone char in the adsorption of derivates phenolics

The bovine bone char (BBC) have received attention by industry of treatment waste water; due to its advantages in front of others adsorbents between these are found: low cost and adsorbent versatility for wide variety pollutants **(Deyder et al., 2005)**. The BBC was prepared in the following way: The bones were cleaned from meat and fat and cut by saw to pieces of approximate size 4-10 cm. Subsequently, bones were washed with tap water for several times. The bones were then transferred to the oven for drying at 353 K. After 24 h, the dried bones were crushed and milled into different particle sizes in the range of 2-3 mm. These particles are burned in an inert atmosphere. This process was carried out in a tubular fixed bed reactor from room temperature to 1073 K for 2 h at a heating rate of 3 K min^{-1} and a flow of N_2 80 cm^3 min^{-1}.

The adsorption from solution depends on the chemical and physical characteristics of the solid as surface area, porosity and surface chemistry, see Table 4. The study about this process has shown dependence with the solution characteristics as pH, ionic strength and temperature **(Moreno-Castilla & López-Ramos M.V., 2007)**. These factors have influence in the adsorption mechanism and in consequence, the magnitude in that the system – (solid-liquid) - liberates heat.

S_{BET} (m^2 / g)	157
Pore Volume (cm^3/g)	0.14
Pore Size (nm)	3.0
Acid Sites (meq/g)	0.23
Basic Sites (meq / g)	0.42
PZC	8.5

Table 4. Physical and chemical characteristics of the BBC

The chemical properties of the adsorbent depends the surface concentration of acid and basic sites, but these are in pH function of solution because the charge on the surface depends of this property. In this study was used 2,4-Dinitrophenol (DNP) a organic compounds commonly used for tincture manufacturing, wood preservatives, explosives, substances for insects control and other chemical products **(Su-Hsia & Ruey-Shin, 2009, Tae Young et al., 2001)** that in aqueous solution can be found as ionic or nonionic species Figure 6.

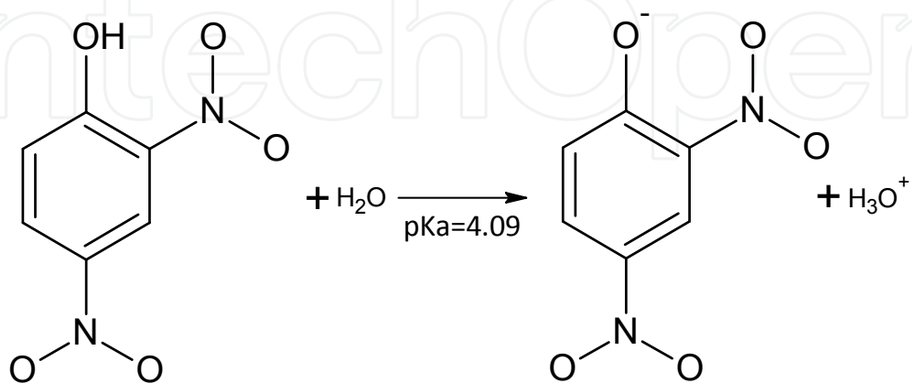


Fig. 6. Species of DNP in aqueous solution.

The adsorption isotherm represents the thermodynamic equilibrium between the adsorbed solute and the solute in solution, the obtained equilibrium data which are used to assess the ability of adsorbent to adsorb a particular molecule.
Figure 7 shows the influence of concentration on the adsorption of DNP on CHB, where the mass of solute adsorbed onto the adsorbent continues to increase when raising the concentration of solute in equilibrium and is not asymptotic at high concentrations.

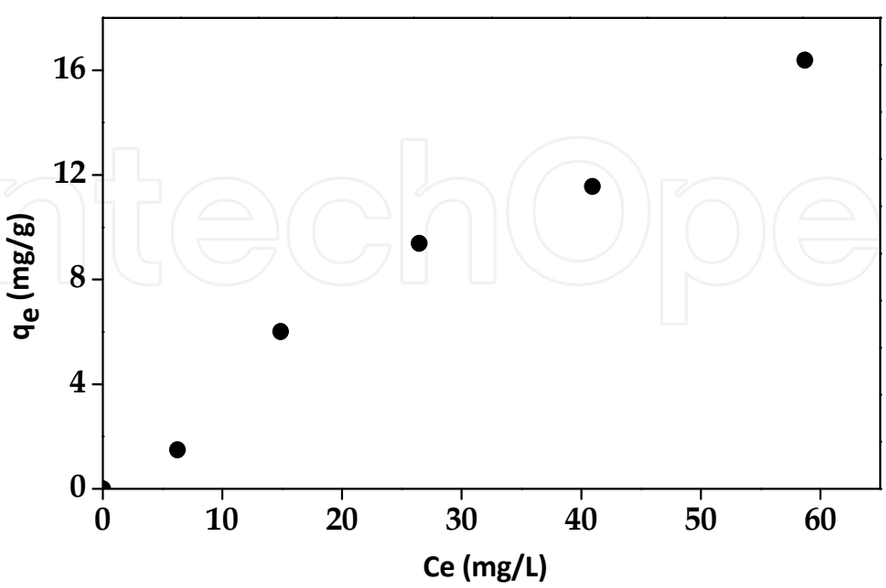


Fig. 7. Adsorption isotherm of DNP on bone char

In the literature on liquid phase adsorption has been reported different mathematical models to represent the adsorption isotherms, the most used are the Langmuir and Freundlich model. The first assumes: (i) uniform adsorption energies on the surface, (ii) no interaction between adsorbed molecules (III) adsorption occurs at specific sites. Meanwhile, the second (I) assumes that the adsorbent surface is energetically heterogeneous, (ii) that increasing the concentration of adsorbate, increases the amount adsorbed on the surface **(Oke et al., 2008, Moreno et al., 2010)**.
These models are represented mathematically as shown in table 5:

Isotherm	Equation	Lineal Form	Graphic
Langmuir	$q_e = \frac{q_m * b * C_e}{1 + b * C_e}$	$\frac{1}{q_e} = \frac{1}{b * q_m}\frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e} vs. \frac{1}{C_e}$
Freundlich	$q_e = k_f * C_e^{1/n}$	$Ln\ q_e = Ln\ k_f + \frac{1}{n} Ln\ C_e$	$Ln\ q_e\ vs.\ Ln\ C_e$

Table 5. Mathematics models of Langmuir and Freundlich.

where q_e is the amount adsorbed at C_e (mg/L), concentration of DNP at equilibrium, b (L/mg), and q_0 (mg/g) are the Langmuir constants related to the energy of adsorption and maximum capacity, respectively; k_f ($mg^{1-1/n}\ l^{1/n}\ g^{-1}$) and 1/n are the Freundlich constants related to the adsorption capacity and intensity, respectively; and q_e (mg/g) is the mass of DNP adsorbed per mass of adsorbent.

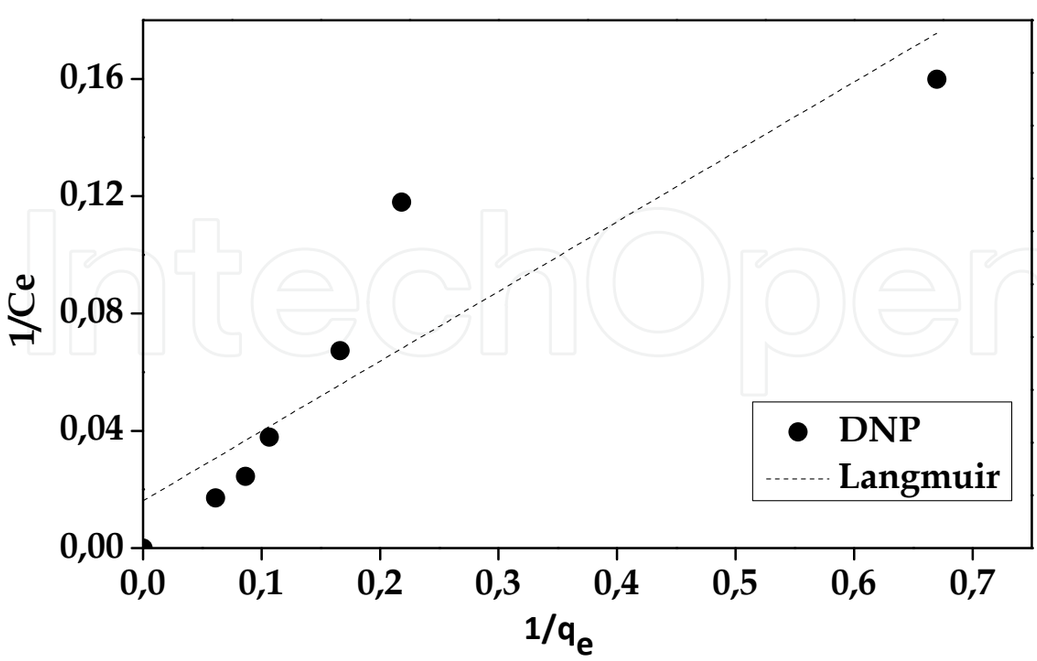


Fig. 8. Adsorption isotherm Langmuir model

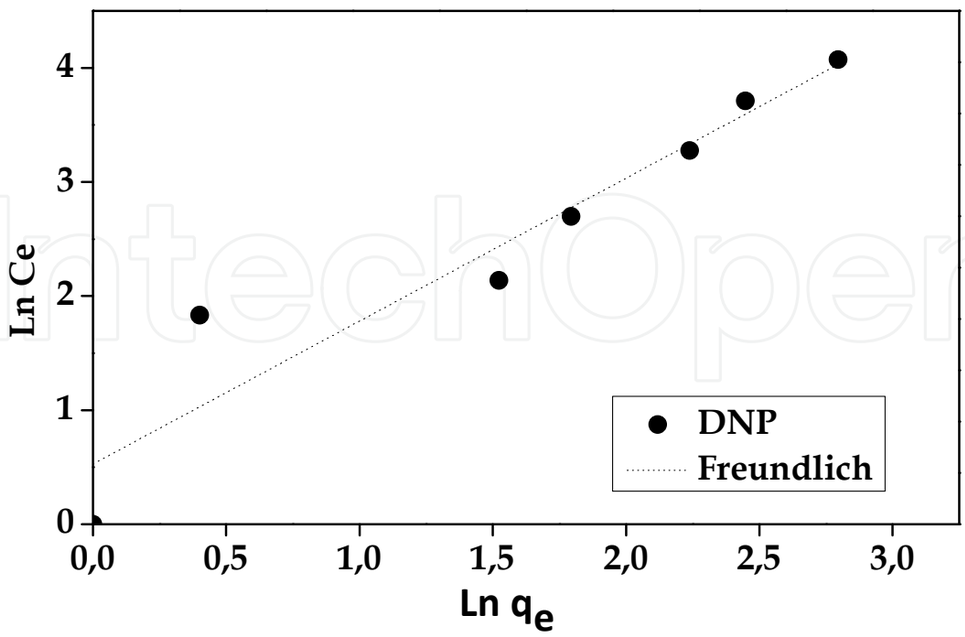


Fig. 9. Adsorption isotherm Freundlich model

Isotherm	Parameter Values
Langmuir	q_m = 61.96
	b = 0.068
	R^2 = 0.7969
Freundlich	K_F = 0.593
	n = 0.798
	R^2 = 0.8907

Table 6. Isotherm parameters for Langmuir and Freundlich models.

Correlating the experimental data of adsorption of DNP on BBC with both models, Figure 8 and 9 shows the typical behavior of the Freundlich isotherm, which contrasts with the parameters and correlation coefficients, see Table 6. This model describes the surface of the adsorbent is energetically heterogeneous and includes the lateral interactions between adsorbate molecules. In this type of liquid-solid systems, it is important understand that when a model fits the experimental data does not support the adsorption mechanism occurs under the principles of the model. Although these data are adjusted by mathematical methods - statistics to calculate the parameters given, these methods do not consider the interactions between adsorbate and surface active sites.

Depending on the thermodynamic conditions of the system, heat is produced when a solid comes into contact with the solution; this intensity is determined by immersion enthalpy. It is set for a specific amount of a solid and measured by a technique known as immersion

calorimetry **(Blanco et al., 2008)**. When make this type of measure, where contact between a solid and a solution is involved, there are different interactions that contribute to the total amount of heat produced. Among these are interactions between water and the groups on the solid's surface, the filling of pores and adsorption on the surface. Furthermore, there are also adsorption of and interactions with the solute; these depend on the characteristics of the solution **(Moreno-Piraján et al., 2007)**.

The values of the enthalpies of immersion were evaluated from the thermograms, where the heat generated by the process of adsorption is proportional to the area under the curve of the peak generated by the thermal effect. Figure 10 shows the typical thermograms for the immersion of BBC in DNP solutions of 10 and 30 mg/L.

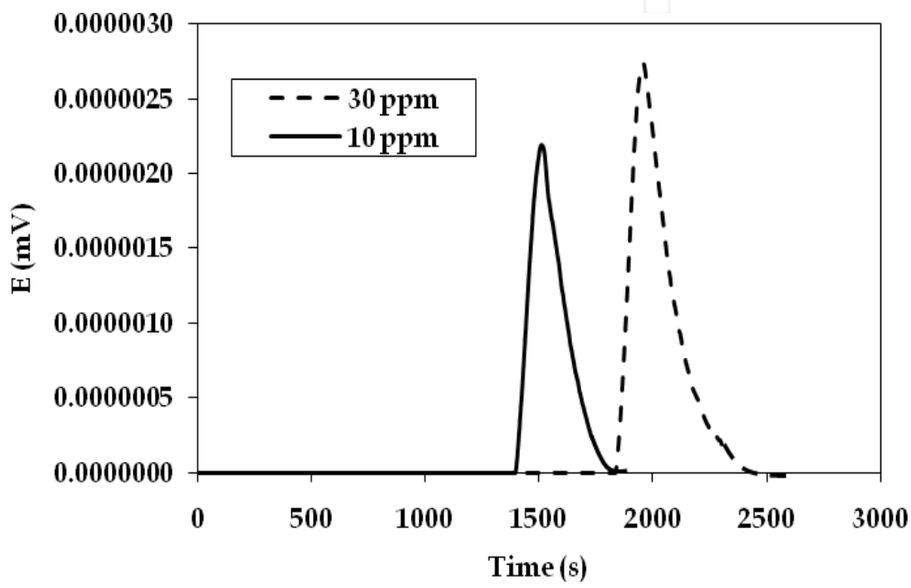


Fig. 10. Thermograms of BBC immersion in a solution of DNP at concentrations of 10 and 30 mg/L at 298 K.

Figure 11 shows the (a) interactions between bone char and DNP in solutions at different concentrations and the (2) interactions with the adsorbate char was obtained subtracting the effect of char-water interactions.

As can be seen in the Figure 11, at low concentrations (10-30 mg/L) there was a greater interaction between the BBC and the adsorbate (DNP); however, as the concentration increased (50-100 mg/L) there was a decrease in enthalpy, i.e. weaker interactions between the adsorbent and the adsorbate.

When relating the enthalpies as a function of adsorbed amount of DNP can be seen that the enthalpy is directly proportional to the percent of retention, this behavior is due to the main morphological characteristic of the material is its heterogeneity, therefore the heat generated is different because that the adsorbate has occupied the most active sites than the immediately occupy.

The differential free energy of adsorption that occurs in the time interval, in which it is carry a calorimetry measure, is determined relating the kinetics of the process to this time interval. Where tinicial is the time in that started the immersion solid-liquid and tfinal is the time in that ended the calorimetric measurement. The free energy difference as a thermodynamic

parameter is the fundamental criterion of spontaneity **(Smiciklas et al., 2008)**, and may be calculated considering the initial concentration (Co) and the concentration in the equilibrium (Ce) to tfinal, by equation (22).

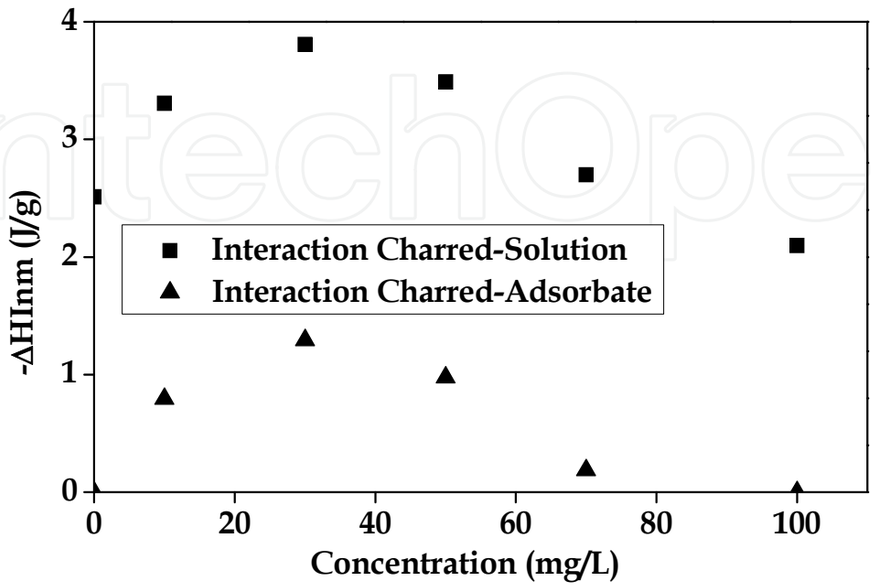


Fig. 11. Enthalpies of immersion of BBC on DNP to different concentration.

$$\Delta G\,|_{ti}^{tf} = -RT\,Ln\left(\frac{C_o}{C_e}\right) \tag{22}$$

Where ΔG (kJ/mol) is differential free energy change; R is universal gas constant, and T (K) is absolute temperature. Reaction occurs spontaneously if G is a negative quantity. From the above equation, the differential change Gibbs free energy for the adsorption process of DNP on BBC to tfinal (293 K) is -113.0 kJ/mol, this negative value indicate that the adsorption of DNP is thermodynamically feasible.

In the specific case of the solution 30 mg/L which has a differential ΔH_{imm} = -56.10 kJ/(g*mol) and substituting the parameters known in equation (23) determine the differential entropy of the process is equivalent to 580 J/(mol K) this positive value suggests that the organization of the adsorbate in the solid-liquid interface and coincide with value obtained for free energy.

$$\Delta S\,|_{ti}^{tf} = \frac{\Delta H_{imm} - \Delta G}{T} \tag{23}$$

Granular activated carbon for adsorption of nickel

The samples used for nickel removal were obtained from a commercial granular activated carbon made from coconut shell GAC, which was oxidized with GACoxN 6M nitric acid, two parts of this sample were treated one at 723 K and another 1023 K under nitrogen atmosphere, GACoxN723 and GACoxN1023, and a final sample obtained by heating the sample at 1173 K GAC, GAC1173, these samples were characterized by N_2 physisorption at -

196 ° C and their surface chemistry by Boehm and determining the point of zero charge, in addition, an immersion calorimetry was conducted in different liquids, such as benzene, carbon tetrachloride and water.

Sample	$Área_{BET}$ m^2/g	Vo cm^3/g	Carboxilic µmol/g	Lactonic µmol/g	Phenolic µmol/g	Acidity Total µmol/g	Basicity Total µmol/g	pzc
GAC	842	0.34	72.2	40.5	85.0	198	90.5	5.4
GACoxN	816	0.35	267	52.4	73.7	393	48.6	3.4
GACoxN723	903	0.32	95.3	60.2	112	268	103	7.9
GACoxN1023	935	0.37	2.36	10.2	47.9	60.5	266	8.2
GAC1173	876	0.35	0.00	11.5	34.9	46.4	278	8.9

Table 7. Physical and chemical parameters of samples

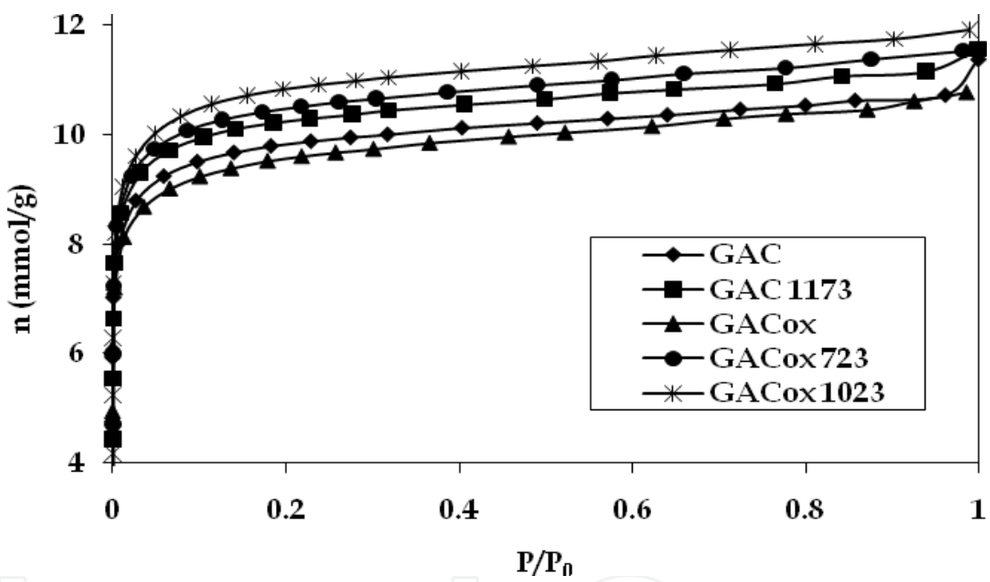


Fig. 12. N_2 adsorption isotherms at 77 K for different samples

The isotherms of nitrogen obtained for each sample are shown in Figure 1. These are classified as type I adsorption isotherms, where a knee at low relative pressures is evidenced, characteristic of microporous solids in accordance with data obtained after applying the Dubinin-Raduskevich equation. It is important to note that the oxidation process caused a decrease in surface area, this is explained by considering that the oxidation with nitric acid promotes the formation of surface oxygenated groups at the edges of the openings of the pores, these groups are mainly carboxylic and carbonyl (**Dias** *et al.* **2007; Daud & Houshamnd. 2010; Yin** *et al.* **2007)** besides producing the collapse of certain porous structures (**Radovic** *et al***. 2000; Yin** *et al***. 2007; Silvestre-Alvero** *et al.* **2009**), additionally, a surface area increase can be observed even in relation to the sample treated with a higher temperature. This is a result of selective removal of surface groups formed in the oxidation processes, which break down into carbon monoxide and carbon dioxide. In other words, with heat treatment more carbon atoms are lost promoting surface area increase in the solid.

On the other hand, we evaluated the changes in surface chemistry of each sample, taking into consideration the important role of surface chemistry on the removal of dissolved metals in aqueous solutions. Table 7 shows the results of the amount of surface groups of each of the samples obtained through Boehm titration. It is observed that the content of acid groups increased by the oxidation treatment, favoring mainly the formation of carboxylic groups, such as reported in other studies (**Gao** *et al***. 2009**). Additionally heat treatment changed the number of groups according to their different thermal stabilities, so, in general it is considered that at low temperatures (about 700 K) and in an inert atmosphere carboxylic groups decompose; in the range of 1000 K lactone groups, carboxylic anhydrides, phenol and ether decomposition is favored; and in higher temperatures up to 1200 K quinone and pyrone groups decompose. On the other hand the values of zero point of charge are consistent with changes in surface chemistry of each sample according to the treatment applied. (**Chingombe** *et al.* **2005; Szymański** *et al***. 2002; Figueiredo** *et al.* **1999; Figueiredo & Pereira. 2010**)

As for the characterization of samples obtained by immersion calorimetry, it is important to note that the enthalpies of immersion allow to evaluate the type of interactions that occur between the solid and the wetting liquid, considering that: if there are no specific interactions between the molecules of the wetting liquid and the solid surface, the immersion enthalpy corresponds to the accessible area of the molecule of the liquid, and if on the contrary, there are specific interactions as in the case of some samples immersed in water, the immersion enthalpy would indicate the hydrophobic or hydrophilic character of the surface of the sample.(**Stoeckli et al. 2001; Szymański et al. 2002**)

Table 8 shows the results obtained by calculating the enthalpies of immersion in benzene, carbon tetrachloride and water. As for the results using molecules with bipolar moments equal to zero it was observed that: the enthalpies of immersion changed according to changes of surface area as shown in Figure 2 and for the oxidized sample, which has a lower surface area, the enthalpy of immersion is less than for the original sample and even for the heat-treated ones in according to what it was discussed in the analysis of nitrogen adsorption isotherms, the same trend was observed for the enthalpies of immersion in carbon tetrachloride, although values were lower in these enthalpies of immersion, this is basically due to the difference in the size of the molecules of each liquid, which for benzene is 0.37 nm and for carbon tetrachloride is 0.66 nm, in other words, the carbon tetrachloride molecule has diffusion restrictions, therefore the interactions involved correspond only to pores in which the molecule does not have this restrictions, this situation does not occur with benzene that is smaller.

Sample	$\Delta H_{ImmC_6H_6}$ (J/g)	ΔH_{ImmH_2O} (J/g)	$\Delta H_{Imm\ CCl_4}$ (J/g)
GAC	-106.4	-49.65	-75.05
GACoxN	-94.98	-66.59	-85.87
GACoxN723	-107.9	-53.32	-50.76
GACoxN1023	-128.8	-37.39	-57.01
GAC1173	-145.1	-32.39	-94.29

Tabla 8. Enthalpies of immersion in Benzene, Carbon Tetrachloride and water.

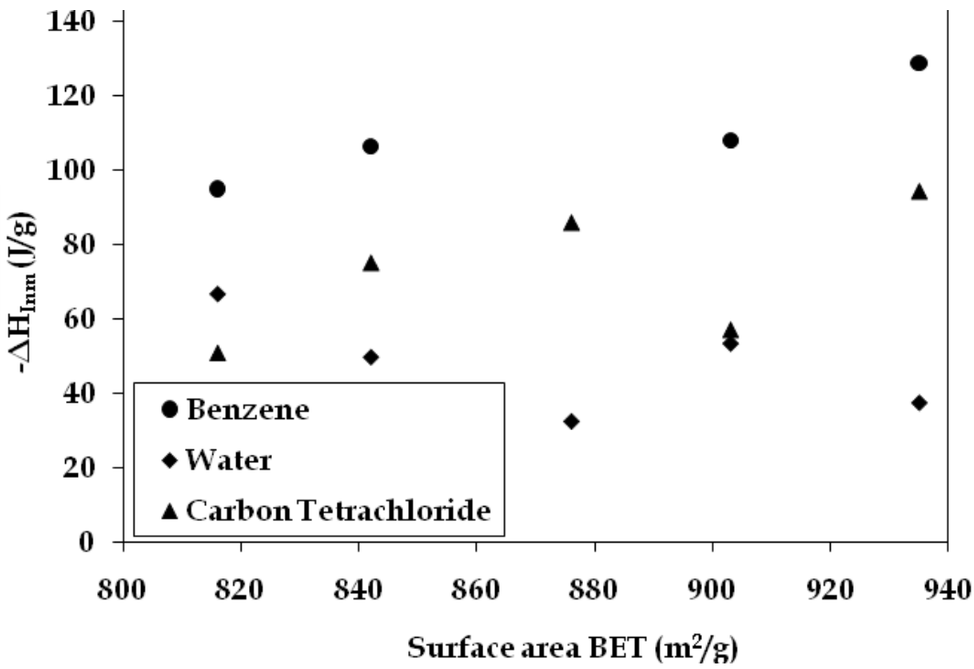


Fig. 13. Enthalpies of immersion in Benzene, Carbon Tetrachloride and water in terms of BET area

On the other hand, the difference in the enthalpies of immersion in water of different samples indicates the change in surface chemistry (**Giraldo & Moreno-Piraján. 2008; López-Ramón** *et al.* **2000**), as a result of the different treatments that samples underwent, that is, the development or removal of surface groups on the surface of the solid, thus, a greater amount of oxygenated surface groups as in GACOx's case which leads to a bigger enthalpy of immersion, as a consequence of the interactions established between the polar molecule as is the water molecule and oxygen surface groups developed in the sample, which is consistent with the chemical characterization, these groups were mostly acid type, specifically carboxyl groups. It is also observed that in thermally treated samples decreased enthalpies of immersion in water due to the selective decomposition of the groups present on the surface and therefore a decrease in specific interactions with the water molecule. Additionally, it is possible to conclude that the interactions of water does not occur exclusively with surface groups of the different samples because the sample CAG1173 in which one would expect to have a minimum amount of oxygenated surface groups, also has an calorimetric effect attributed to interactions dispersive type and non- specific type. As for the hydrophobic character of the surface is found that this decrease with the oxidation process and gradually increases with the heat treatments, being higher in the sample treated at 1173 K. Figures 14 and 15 shows the typical thermograms, obtained in the immersion of a solid in the different liquids used. These two figures were chosen because you can see the difference in magnitude of the peaks corresponding to each liquid for to the most oxidized sample (GACoxN) and sample treated to highest temperature in an atmosphere inert (GAC1173).

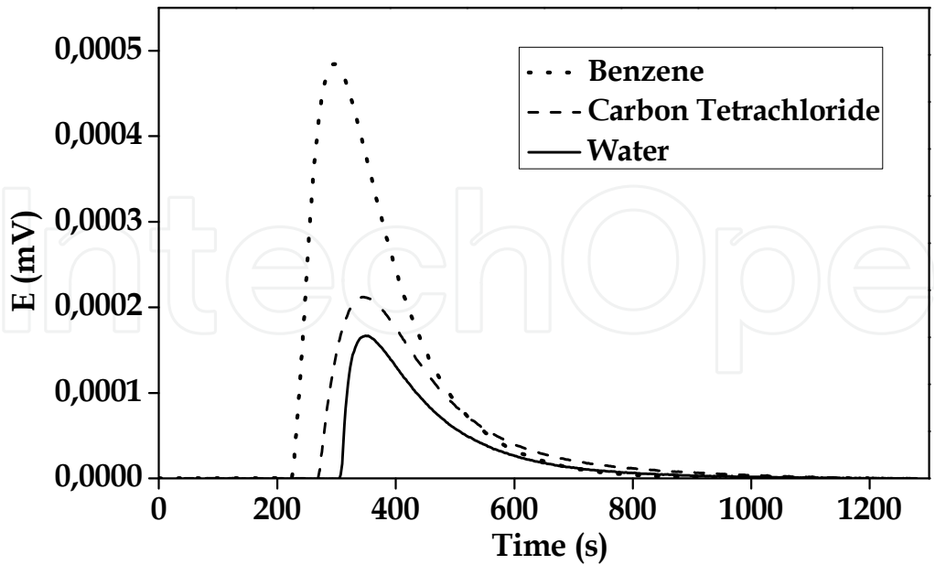


Fig. 14. Thermogram of Immersion Calorimetry in Benzene, Carbon Tetrachloride and water of GAC1173 sample

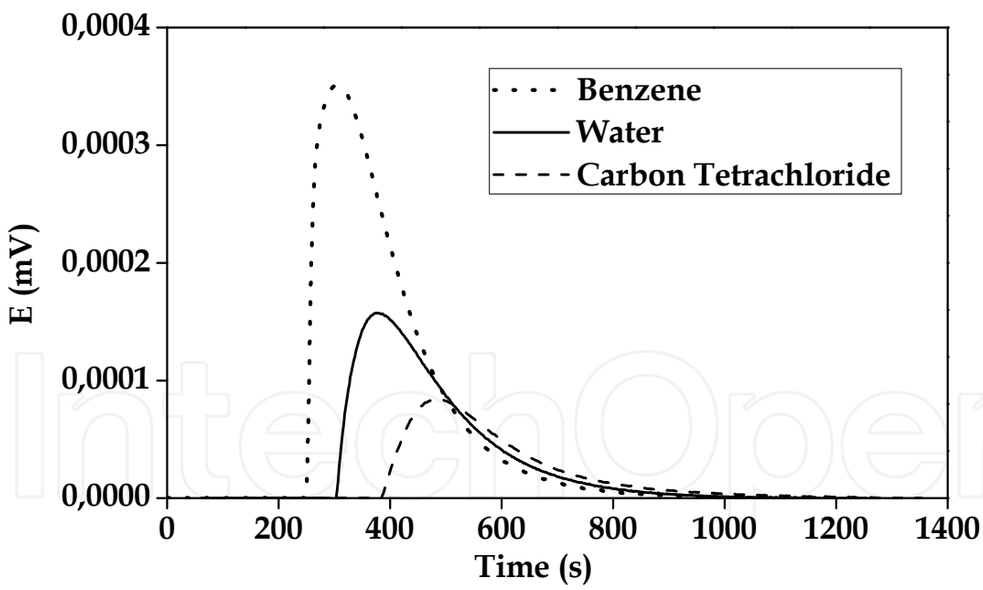


Fig. 15. Thermogram of Immersion Calorimetry in Benzene, Carbon Tetrachloride and water of GACoxN1173 sample

Finally, the samples were used for the removal of nickel from aqueous solution, for this, 0.500 g of each sample were put in contact with 50ml of the nickel solution of concentrations from 100 to 500 mg /L, initial pH of the mixture was adjusted to 6, taking into account that in this pH is nickel is found as Ni (II). The experimental data obtained in the adsorption process were adjusted to the Redlich-Peterson model and are shown in Figure 16.

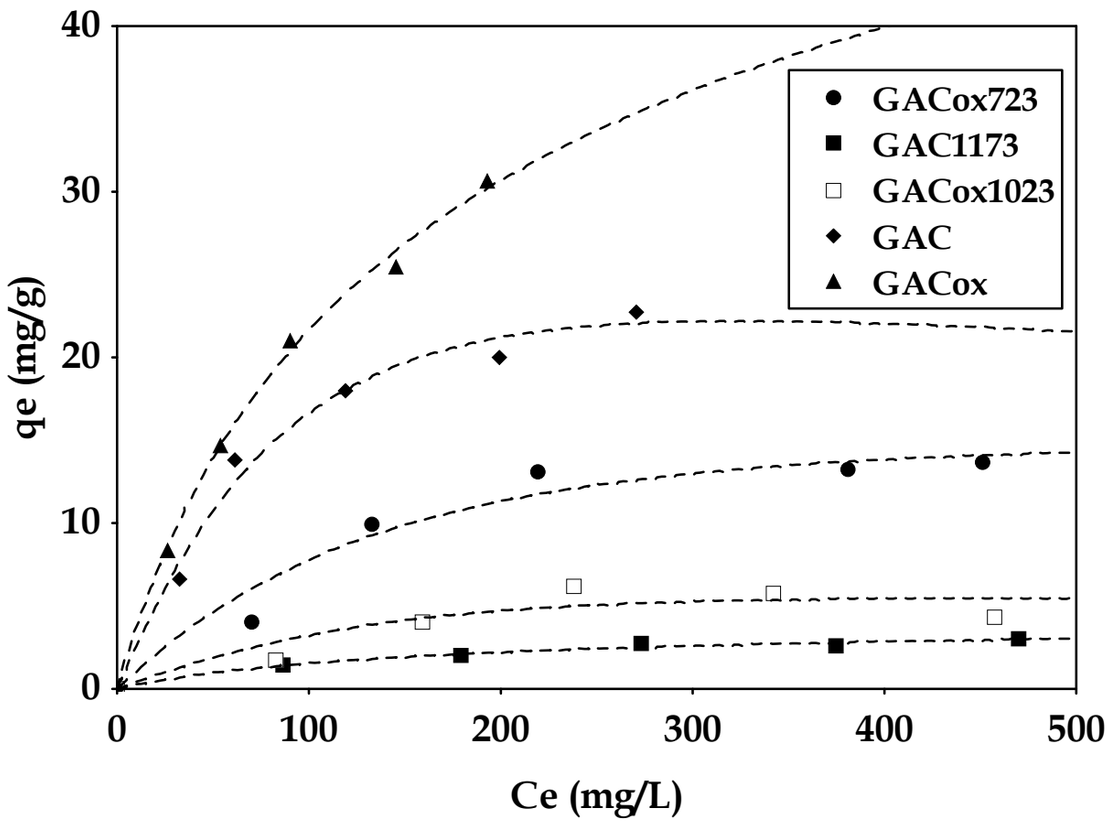


Fig. 16. Adsorption isotherm of Nickel on different samples fit the Redlich-Peterson model.

The importance of the role of oxygenated groups on the activated carbon surface in the adsorption process of ions from aqueous solution has been highlighted by many authors (**Puziy** *et al*. **2002**). It is generally considered that the removal of an ion is mainly attributed to the interaction of surface groups and the ion, through various mechanisms, such as: formation of metal complexes like COOH-M and / or donor-acceptor reactions of electrons (**Petit et al. 2010; Moreno-Castilla** *et al.* **2010**), that is, by establishing specific interactions, therefore, these mechanisms are favored when the solid undergoes an oxidation process as in the case of the sample GACoxN, which has a higher adsorption capacity with respect to other ones, this capacity decreased in heat-treated samples after the process oxidation ratifying the importance of the presence of oxygenated surface groups, although it is important to note that the adsorption capacity of GAC1173 sample is lower, it is also suggested to contemplate within the mechanisms of adsorption interactions that are not only specific but also of the dispersive type, to a lesser extent but to complement the adsorption process.

Activate carbon for the adsorption of phenol

Among various industrial waste to generate contamination there are tires, this waste is a difficult material to degrade and handle due to its physicochemical composition, generating a problem of global nature. Therefore alternatives different have been proposed for reuse, among these are energy production through incineration, combustion, and pyrolysis

processes. (**Nadem et al. 2001**) Another alternative that being studied at present is the production of activated carbon from this waste, there by creating a double benefit for the environment.

A study was conducted about to granular activated carbon adsorbents prepared from tires. To this end, the tires were cut into pieces with a size of 10 mm thick, two samples were treated with phosphoric acid at 20 and 40% p/p (TCP20 and TCP40) and other samples were treated with potassium hydroxide to the same concentrations (TCK20 And TCK40), then underwent to a carbonization process in a horizontal furnace at 1123 K for 2 hours. In this way is prepare by physical activation with CO2, samples were subjected to a pyrolysis process with N2 at 923 K, and then activation with CO2 at two temperatures 1123 K and 1223 K (TCCO2-1123 and TCCO2-1223) during 2 hours. All samples were characterized by N2 adsorption at 77 K and immersion calorimetry in benzene. Some of the results obtain are compiled in Table 9.

Samples	SBET (m^2/g)	Vo DR (cm^3/g)	Eo (KJ/mol)	$-\Delta H_{imm}$ C_6H_6 (J/g)
TCP20	71.17	0.018	13.59	5.670
TCP40	52.85	0.013	13.62	3.120
TCK20	149.2	0.068	19.95	35.55
TCK40	157.3	0.070	19.63	26.17
TCCO2-850	25.44	0.009	14.23	11.48
TCCO2-950	58.12	0.020	14.92	21.36

Table 9. Characteristics of the samples obtained by gas adsorption and immersion calorimetry

Figure 17 shows the adsorption isotherms for three coals of the series prepared. the TCK40 sample presents a type I isotherm according to IUPAC classification, feature of microporous carbons, the samples and TCCO2-1223 and TCP20 have type II isotherms characteristic of mesoporous carbon, where adsorption occurs in open surface with the formation of multilayers. (**Martín-Martínez 1988**)

Immersion calorimetry as mentioned along this chapter, allow complement the characterization of porous materials. Figure 18 shows the thermograms obtained for the immersion of the samples in benzene, which is a liquid of wet to assess the area accessible to the molecule. It is observed that the highest enthalpies are obtained for samples prepared with sodium hydroxide which is consistent with the surface areas of these samples. By contrast the samples activated with phosphoric acid have low values compared with those activated with CO_2, probably due to the presence of phosphorus compounds in activated carbon, which prevents the access of the benzene molecule. (**Marsh & Rodríguez-Reinoso. 2007**)

From Dubinin Radushkevich equation was calculated pore volume and the characteristic energy for the samples.

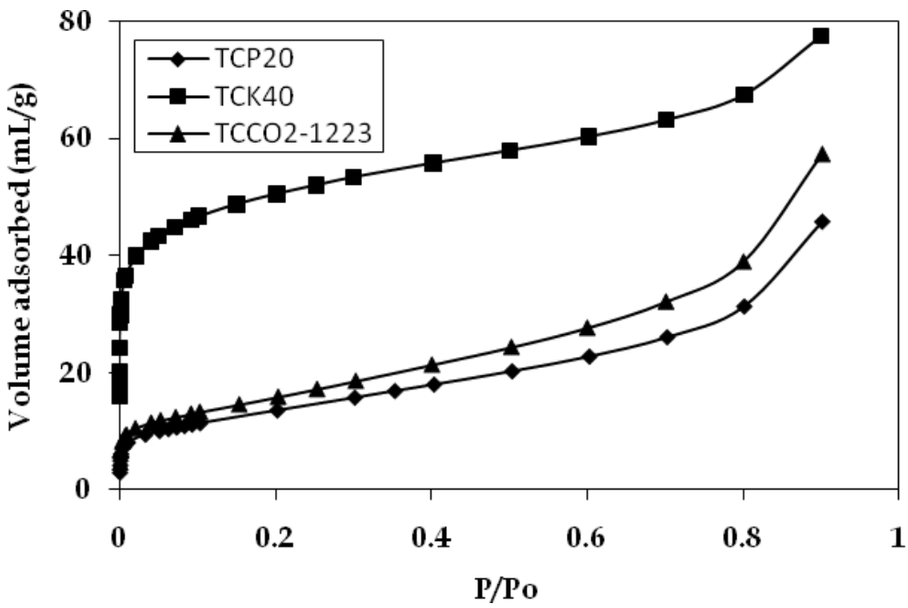


Fig. 17. Isotherms of N_2 of the samples TCP20, TCK40 y TCCO2-1223

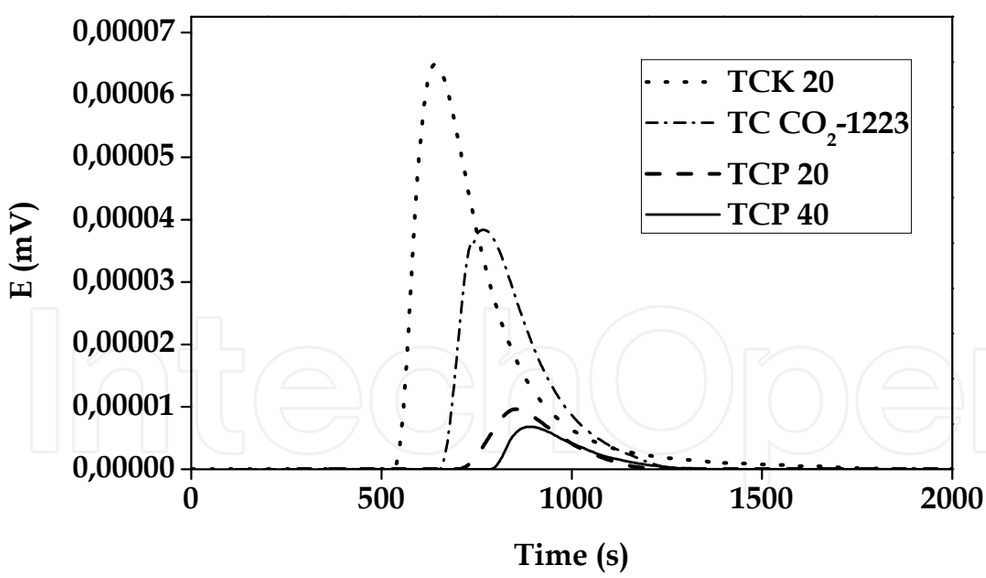


Fig. 18. Thermograms obtained for the samples.

$$\ln V = \ln V_o - D\left(\ln \frac{P_o}{P}\right)^2 \tag{24}$$

Where V is the volume adsorbed at certain pressures, P/Po is the partial pressure, Vo is the micropore volume and D is a constant. **Bansal et al. 1988**

Figure 19 shows the graphs of DR for the samples TCK40 and TCK20 where you can see that a deviation from linearity near the saturation pressure, explaining that he has a multilayer adsorption and capillary condensation in mesopores **(Martín-Martínez 1988)** consistent with the isotherms of N_2 obtained which present a mesoporosity of activated carbons.

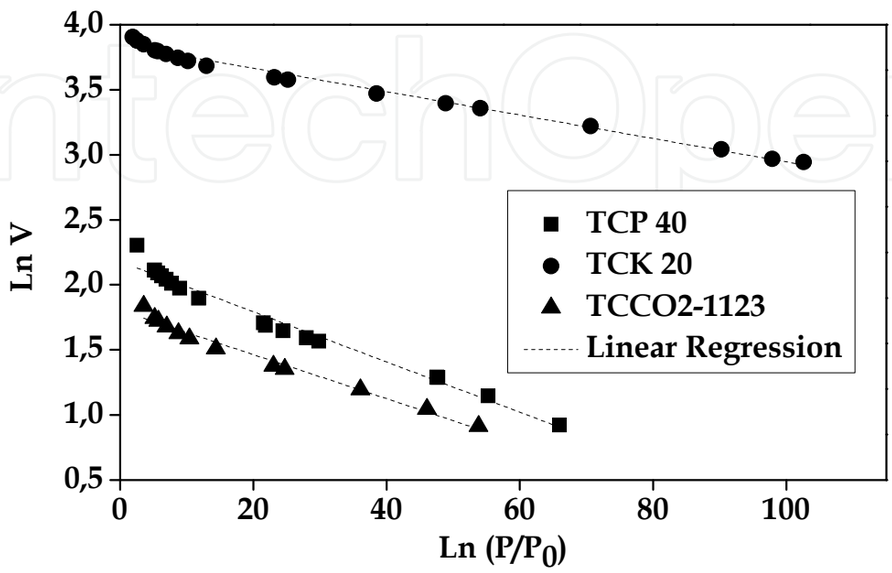


Fig. 19. The graphs of DR for the samples. Organized as follows way TCP40-TCK20-TCCO2-1123.

From of the constant D to be the slope of the graph permit to calculate the characteristic energy of adsorption given by the following equation:

$$\ln V = \ln V_o - D\left(\ln \frac{P_o}{P}\right)^2 \tag{24}$$

$$E_o = \frac{RT}{\sqrt{D}\beta} \tag{25}$$

Where R is the gas constant, 80414J/mol, T is the critical temperature of liquide nitrogen, 77K and β is the affinity coefficient of nitrogen, 0.34.

Stoeckli and Krahenbüehl were the first to correlate the enthalpy of benzene with the microporous parameters, in this work is realized this correlation but for mesoporous carbons. Figure 20 relates the characteristic energy of the nitrogen molecule with the enthalpy of immersion of the benzene molecule. In the activated carbons with carbon dioxide and potassium hydroxide gives a higher characteristic energy to a higher enthalpy of immersion, unlike those activated with phosphoric acid, which has a decrease in enthalpy with increasing energy feature, this behavior shows proportionality existing between the enthalpy of benzene and energy characteristic of N_2, despite being two different methods to perform. Samples with higher BET surface area have a higher enthalpy of immersion in benzene which is the expected behavior because it has a greater surface arranged to interact with benzene **(Silvestre-Albero et al.2004).**

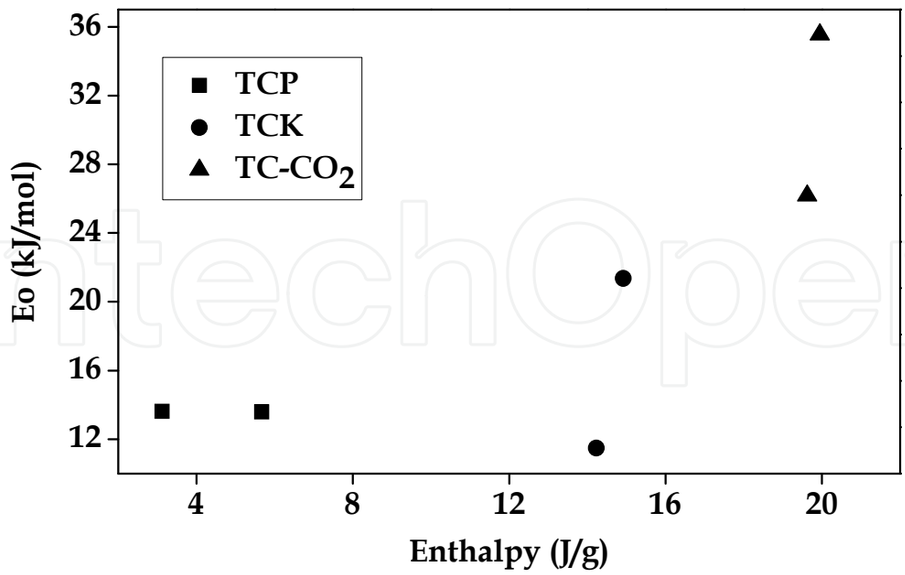


Fig. 20. Relación entre la entalpía de inmersión y la energía característica del nitrógeno.

Activated Carbon monoliths for CO2 adsorption

Taking into account the interest they have taken the activated carbon monoliths in recent years, and its potential use in gas adsorption, is being developed in the research group work which seeks to make a contribution to knowledge of chemistry of solid adsorbents through the preparation, characterization and functionalization of carbon materials granular and monolithic type contribute to the study of the process of adsorption / gas capture a high environmental interest such as carbon dioxide. The CO_2 adsorption, has been studied as a way to retain the gas and check for interactions and conditions that govern the process to be more efficient and better use, the problem with CO_2 is not simple reason that alternatives are sought treatment with new materials, which will open avenues and possibilities according as knowledge of processes such as adsorption is broader.

As a preliminary approach to the preparation of carbonaceous materials of potential interest in the CO_2 adsorption, has been carried out the preparation of activated carbon monoliths disk type take taking advantage of two materials source lignocellulosic s generated as waste in large quantities in Colombia; coconut shell (samples COD) and African palm stone (samples CUD), the endocarps of these precursors are impregnated with H_3PO_4 solutions at different concentrations for a period of 2 hours at 358K, then take a uniaxial press, where the shaping is done by pressing at 423 K, structures are then carbonized in a horizontal furnace at a linear heating rate of 1 $Kmin^{-1}$ to a temperature of 723K remaining there 2 hours. Finally, the monoliths obtained are washed with hot distilled water until neutral pH to remove any traces of chemical agent used in the impregnation **(Rodriguez-Reinoso et al., 2004, Vargas et al., 2010)**.

Subsequently, textural, chemical and energy characterization of monoliths is performed to establish their behavior. The adsorption isotherms of N_2 at 77K and CO_2 at 273 K are determined, the experimental data fit the Langmuir model, and further immersion calorimetry in benzene are performed (0.37 nm) to establish energy correlations.

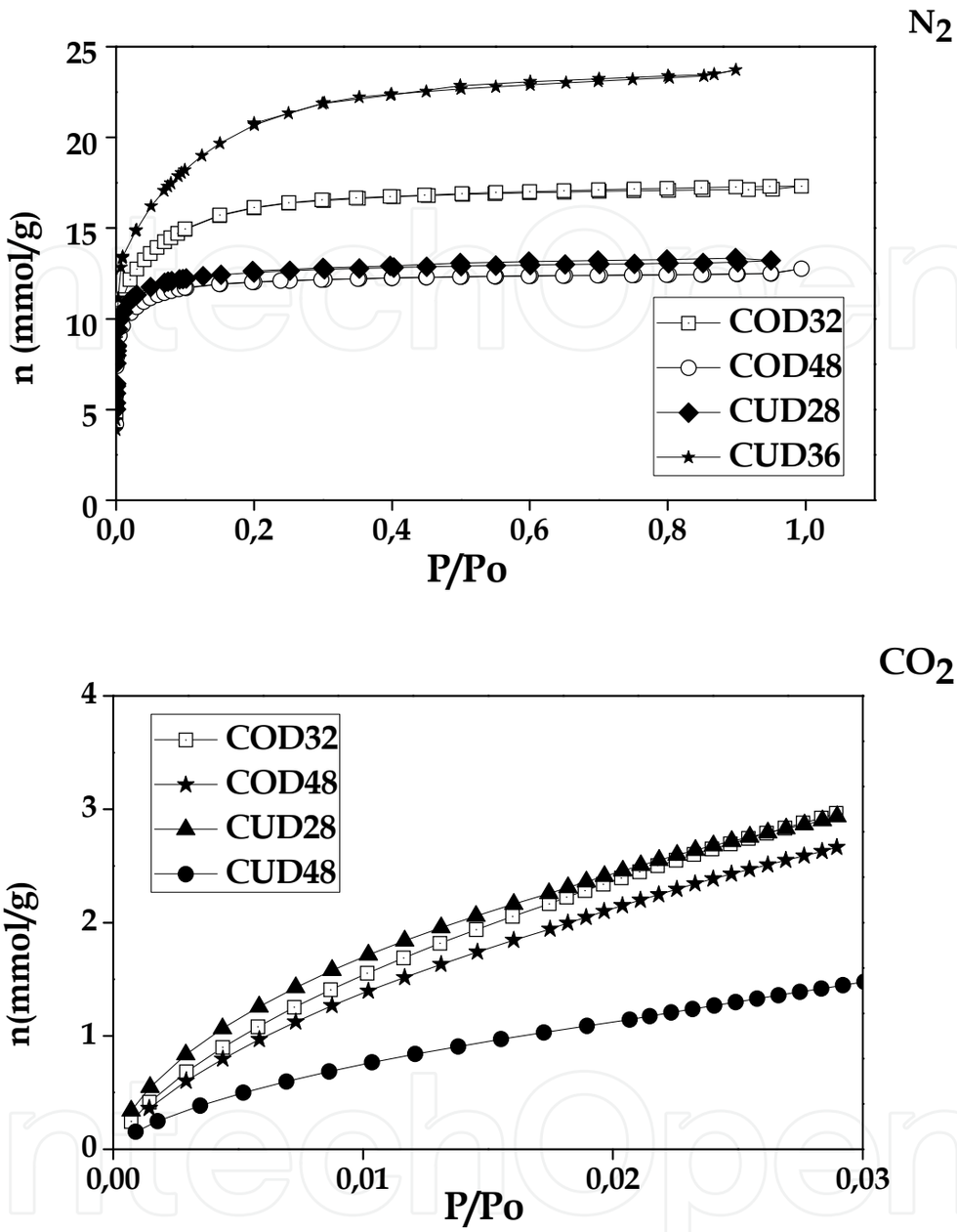


Fig. 21. Nitrogen adsorption isotherms at 77K and CO_2 at 273K for the monoliths with high and low adsorption capacity, with each precursor.

Some of nitrogen and carbon dioxide isotherms obtained for disks are shown in Figure 22, is evidence the obtaining of microporous solids fact is justified by the form type I isotherms, these solids have a surface area between 975 and 1711 m^2g^{-1} and n_o between 11.49 and 18.02 mmol, experimental results indicated that the monoliths prepared from African palm stone have higher adsorption capacity and therefore a larger surface area, further shows that the change in the concentration of H_3PO_4 produces a greater effect on the textural characteristics of samples CUD compared with the COD.

The obtained carbon monoliths were tested as potential adsorbents for CO_2 finding a retention capacity between 88-164 $mgCO_2g^{-1}$ at 273K and atmospheric pressure, in Figure 22 to observe the isotherms of the samples with higher and lower CO_2 adsorption capacity in each series, the monoliths with a better performance in the retention of this gas were COD32 and CUD28.

The table 10 compiles the characteristics of the carbon monoliths prepared, show the data obtained for the interaction of three molecules of interest in the characterization of materials. Additionally, adsorption data were used for the calculation of three parameters: n_{oDR}, n_{mL}, K_L which are measures of the adsorption capacity.

Sample	N_2		CO_2				C_6H_6	
	S_{BET} (m^2/g)	n_o	n_o	n_m	K	E_O (KJ/mol)	$-\Delta H_{imm}$ (J/g)	E_O (KJ/mol)
COD28	1270	14.19	4.88	6.95	0.029	16.01	130	20.90
COD32	1320	13.86	5.10	6.64	0.031	16.87	147	24.03
COD36	1318	14.15	4.91	6.56	0.035	16.80	132	21.33
COD48	975	11.49	4.75	4.75	0.055	18.58	112	22.43
CUD28	1013	12.12	4.93	5.36	0.054	19.12	123	21.47
CUD32	1397	13.35	4.38	6.87	0.028	16.76	130	21.12
CUD36	1711	18.02	2.92	4.53	0.027	16.85	120	14.80
CUD48	1706	18.65	2.36	3.99	0.025	17.63	96	11.48

Table 10. Characteristics of carbon monoliths.

Figure 22 shows the relationship between the number of moles of the monolayer determined by two different models, n_m by the Langmuir model and n_o calculated from Dubinin Raduskevich, shows that the data are a tendency for both precursors although they are calculated from models with different considerations. There are two points that fall outside the general trend CUD28 and COD32 samples, which despite having the highest value of n_o in each series not have the highest n_m

The Dubinin Raduskevich equation is use to determinate, the characteristic adsorption energies of N_2 and CO_2 (Eo) for each samples, likewise by the Stoeckli y Krahenbüehl equation (equation 14) was determined benzene (Eo), in Figure 23 shows the relationship between the characteristic energies determined by two different characterization techniques and found two trends in the data which shows the heterogeneity of carbonaceous surfaces of the prepared samples. The characteristic energy of CO_2 adsorption, is lower in almost all the monoliths compared to Eo of immersion in benzene, this is consistent considering that due to the size of the CO_2 molecule 0.33 nm, this can be accessed easily to narrow pores,

while benzene has a size of 0.37 nm for slit-shape pores and 0.56 nm for cylindrical restricts its accessibility and generates an increase in Eo. In Figure 19a shows that the COD samples show a trend, except COD32 which again leaves the general behavior, this can be attributed to the monolith has a narrow micropores limits the interaction with the benzene molecule, generating a higher Eo.

In the case of samples CUD48 and CUD36 which present a larger surface area, there is a greater more CO2 Eo compared to benzene Eo, in these samples increased the concentration of chemical agent degrades carbonaceous matrix producing a widening pore that provides access to benzene and leads to a decrease in Eo.

Figure 24 relates the characteristic adsorption energy in benzene with the immersion enthalpy in this molecule, can be observed for most samples an increase of the immersion enthalpy with the characteristic energy of the process, which is consistent since the characteristic energy is a measure of the magnitude of the interaction between the solid and the adsorbate is ratified with the increase of enthalpy value.

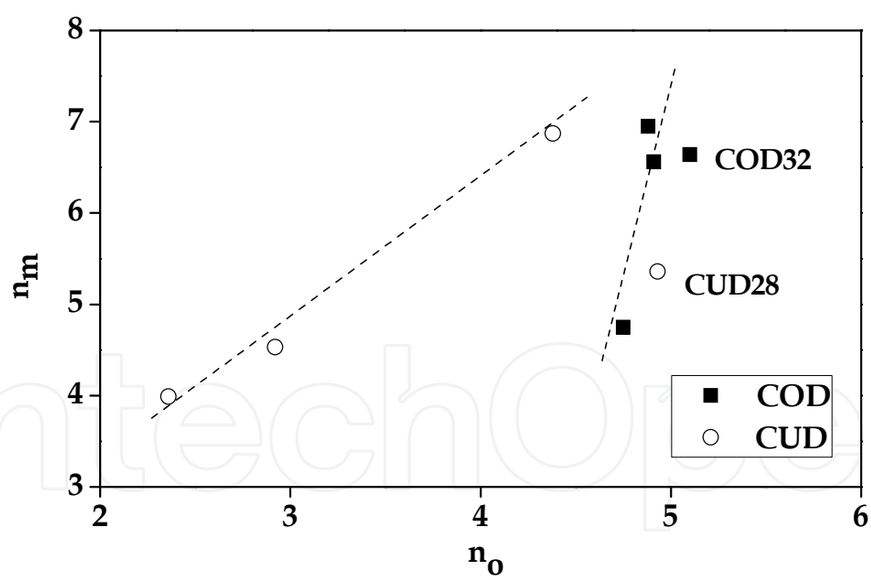
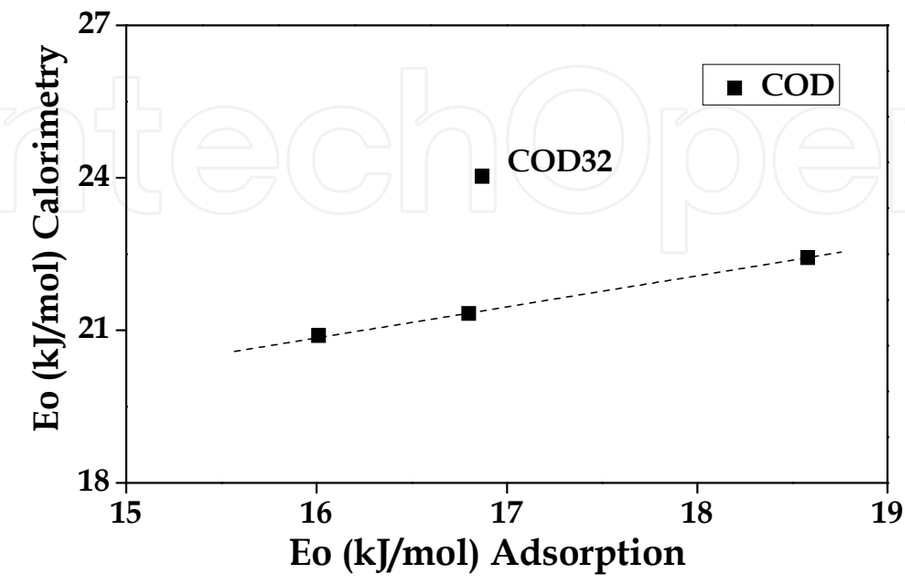


Fig. 22. Relationship between n_m and n_o samples of each series.



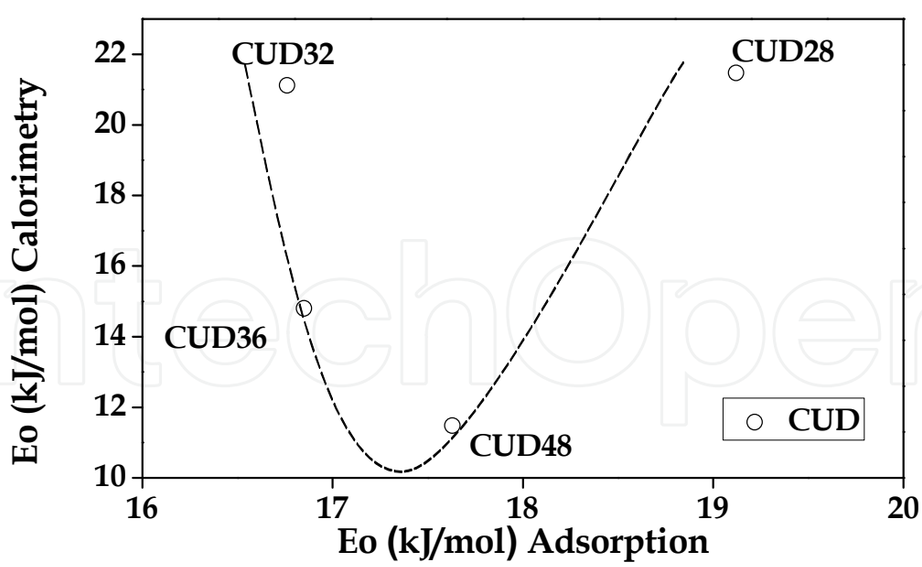


Fig. 23. Relationship between the characteristic immersion energy of benzene and the characteristic adsorption energy of CO_2.

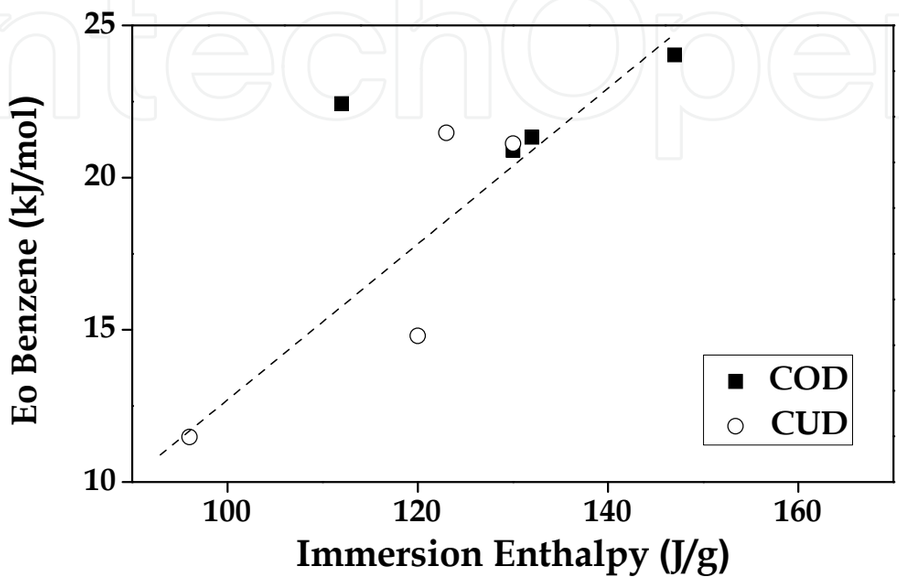
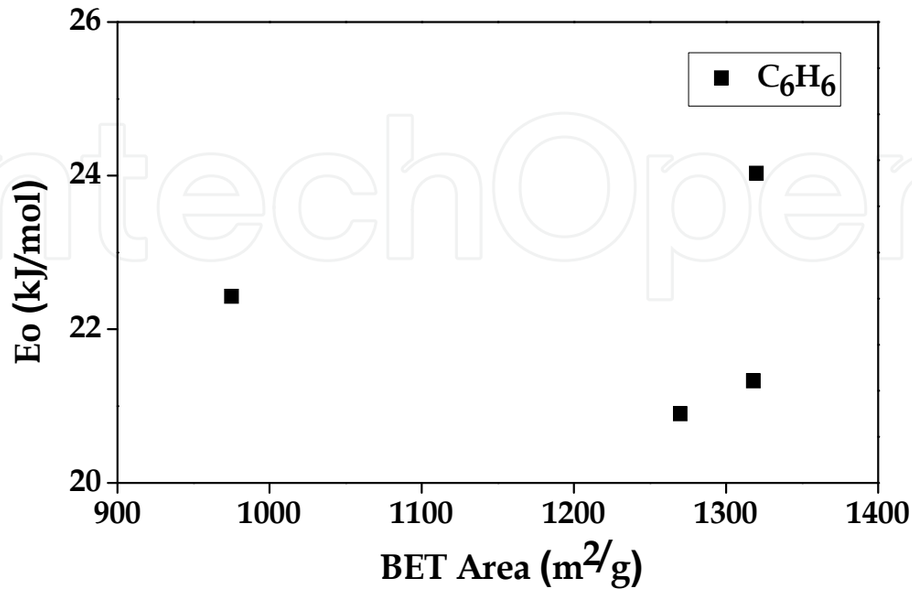
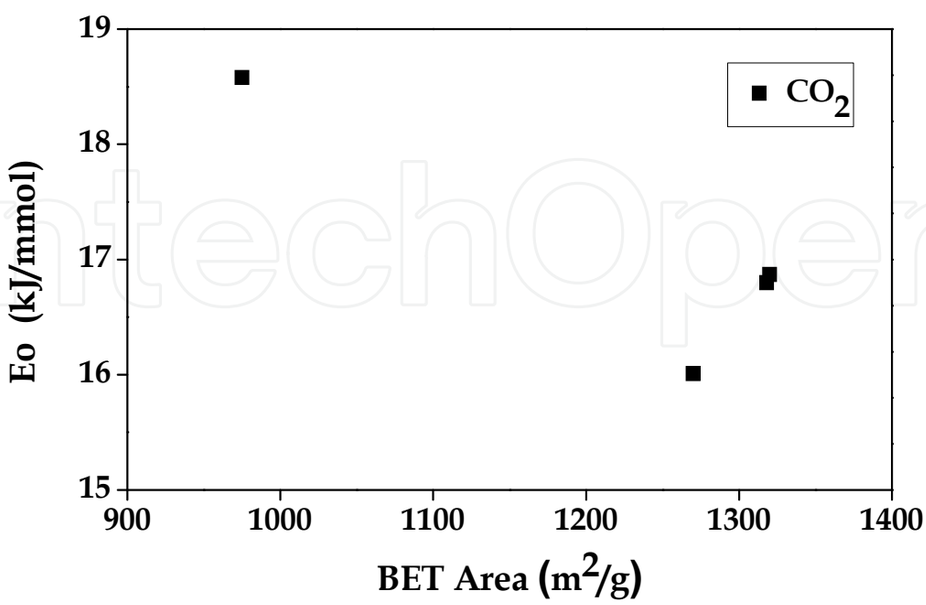


Fig. 24. Relationship between the characteristic adsorption energy in benzene and the immersion enthalpy.

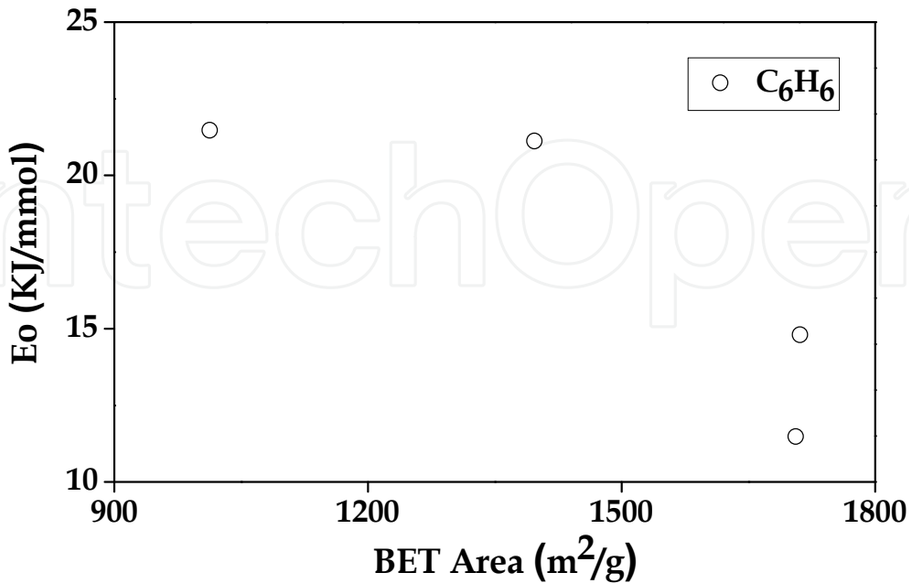
Additionally, establishing correlations between energetic parameters determined by different models and textural characteristics, figure 25 a) and b) show the relationship between the characteristic energy and BET area of the COD samples, different behaviors can be observed for each molecule, in the case characteristic adsorption energy of benzene shows a decrease with increasing area of the discs for samples COD28, COD48, but there was an increase in the COD36 and COD32 samples with higher values for surface area. To CUD, as shown in Figure 25 c) and d) in the case of benzene adsorption, for all samples shows a decrease in Eo. The characteristic adsorption energy carbon dioxide molecule shows a decrease with increasing the BET area, for COD32, COD36 there is a slight increase in Eo attributed to these samples have more narrow micropores that can be seen in the value of n_o CO_2. A similar trend shows the CUD discs; the decrease in the characteristic energy with increasing surface area of the monoliths is related to the increased amount of mesopores in the material, since the adsorption energy decreases with increasing pore size (**Stoeckli et al., 1989**).


26
24
22
20
Eo (kJ/mol)
900
1000
1100
1200
1300
1400
BET Area (m2/g)
C6H6

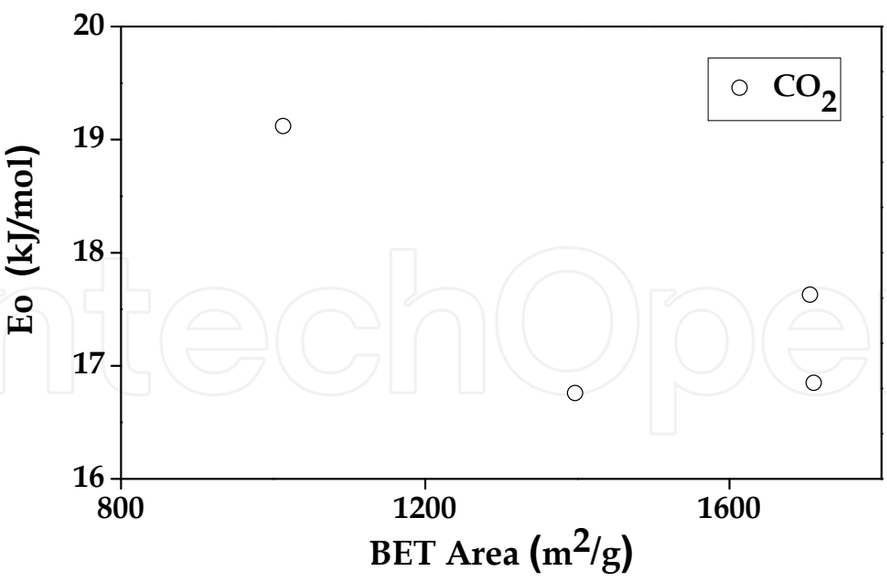
a)


19
18
17
16
15
Eo (kJ/mmol)
900
1000
1100
1200
1300
1400
BET Area (m2/g)
CO2

b)



c)



d)

Fig. 25. Relationship between the characteristic energy and BET area of the series. a,b) COD. c,d) CUD.

2. References

Aydin, Gokhan., Karakurt, Izzet., Aydiner, Kerim. (2010). Evaluation of geologic storage options of CO2: Applicability, cost, storage capacity and safety. *Energ Policy*, Vol. 38, No. 9, pp. 5072-5080.

Bansal R. C., Goyal M. (2005). Activated carbon adsorption. Taylor & Francis Group.ISBN: 0-8247-5344-5 New York, United States. pp.487 .

Bansal, R.C., Donnet, J. B., Stoeckli, H. F. (1988). Active Carbon, Marcel Dekker, ISBN 92-828-5537-6, New York, United States.

Blanco, D., Giraldo, L., Moreno, J. C. (2008). Resorcinol adsorption from aqueous solution on activated carbon. Relation adsorption isotherm and immersion enthalpy, *Revista Colombiana de Química*, Vol. 37, No. 2, pp. 203-216.

Blanco, J., Ávila, P., Martin, M.P. (2000). Honeycomb monoliths of activated carbons for effluent gas purification. *Micropor. Mesopor. Mat*. Vol. 37, No. 1-2, pp. 201-08.

Callister, W. D. (2007). Introducción a la ciencia e ingeniería de los materiales, Editorial Reverté, Vol. 1, Tercera edición, ISBN 978-84-291-7252-2, Barcelona, España.

Carlson, Annelie. (2003).Energy systems and the climate dilemma Reflecting the impact on CO_2 emissions by reconstructing regional energy systems, *Energ Policy,* Vol.31, No. 10, pp. 951–959.

Chingombe, P., Saha, B., Wakeman, R.J. (2005) Surface modification and characterisation of a coal-based activated carbon. *Carbon*.Vol..43*, No. 15*, pp 3132-*3143.*

Daud, W., Houshamnd, A.H. (2010) Textural characteristics, surface chemistry and oxidation of activated carbon. *Journal of Natural Gas Chemistry.Vol. 19, No.3, pp 267-279*

Denoyel, R., Fernandez-Colinas, J., Grillet, Y., Rouquerol, J. (1993). Assessment of the surface area and microporosity of activated charcoals from immersion calorimetry and nitrogen adsorption data. *Langmuir,* Vol. 9, No. 2, pp.515-518.

Deydier, E., Guilet, R., Sarda, S., Sharrock, P. (2005). Physical and chemical characterisation of crude meat and bone meal combustion residue: "waste or raw material?", *J. Hazard. Mater*., Vol. 121, pp. 141–148.

Dias, J.M., Alvim-Ferraza, M.C.M., Almeida, M.F., Rivera-Utrilla, J., Sánchez-Polo, M. (2007) Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. *Journal of Environmental Management*.Vol. 85*, No. 4*,pp. 833-*846*

Dubinin, M. M. (1975). Progress in Surface and Membrane Science, Academic Press, Edited by Cadenhead D. A., Vol. 9, ISBN 0-12-571809-8, New York, United States.

Figueiredo, J.L., Pereira, M.F.R. (2010) The role of surface chemistry in catalysis with carbons *Catalysis Today Vol. 150,No. 1-2, 26 pp 2-7*

Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A., Órfão, J.J.M. (1999). Modification of the surface chemistry of activated carbons. Carbon, Vol. 37*, No. 9*, pp. *1379-1389*

Gao, Z., Bandosz, T.J., Zhao, Z., Hand, M., Qiu, J. (2009) Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes. *Journal of Hazardous Materials*. Vol.167*, No. 1-3*, pp *357-365.*

Garcia-Cuello, V., Moreno-Piraján, J. C., Giraldo-Gutiérrez, L., Sapag, K., Zgrablich, G. (2008). Determination of Differential Enthalpy and Isotherm by Adsorption Calorimetry. *R. Lett. Phys. Chem*., 4 pp.

Garcia-Cuello, V., Moreno-Piraján, J. C., Giraldo-Gutiérrez, L., Sapag, K., Zgrablich, G. (2009). A new microcalorimeter of adsorption for the determination of differential enthalpies. *Micropor. Mesopor. Mat*. Vol. 120 No. 1, pp. 239–245.

Giraldo, L., García-Cuello, V., Moreno-Piraján, J. C. (2008). Caracterización superficial en fase gas y líquida de carbones activados. *Rev.Ing.Universidad de los Andes*, Vol. 27, No. 1, pp. 7-16.

Giraldo, L., Moreno, J.C. (2008) Pb(II) and Cr(VI) adsorption from aqueous solution on activated carbons obtained from sugar cane husk and sawdust. *Journal of Analytical and Applied Pyrolysis*, Vol. **81, No.** 2, pp 278-284.

Hemminger, W. & Höhne, G. (1984). Calorimetry: Fundamentals and Practice, Verlag Chemie, ISBN 2-87352-027-2, Florida, United States.

Jiménez, O. (2000). Preparación de carbón activado a partir de distintos tipos de material vegetal colombiano de desechos con posible aplicación en la remoción de fenol en agua residuales, Trabajo de Grado. Departamento de Química. Universidad Nacional de Colombia. Bogotá, Colombia.

Kraus, G. (1955). The heat of immersion of carbon black in water, methanol and n-hexane. *J. phys. Chem*. Vol. 59, No. 4, pp. 343-345.

Llewellyn, P. L. & Maurin, G. (2005). Gas adsorption microcalorimetry and modelling to characterize zeolites and related materials, *C. R. Chim.*, Vol. 8 No. 1, pp. 283–302.

López-Ramón, M.V., Stoeckli, F., Moreno-Castilla, C., Carrasco-Marín, F. (2000) Specific and non-specific interactions of water molecules with carbon surfaces from immersion calorimetry. *Carbon*. Vol. 38*, No. 6*, pp.825-*829.*

Marsh, H., Rodriguez-Reinoso, F.(2007) Encyclopedia of Materials: Science and Technology. Activated Carbon. 542 p.

Marsh, Harry., Rodriguez-Reinoso, Francisco. (2006). Activated Carbon (Origins). En: Activated carbon, Elsevier Science Ltd ISBN: 0080444636, pp. 13-81.

Martin Matinez, J.M. (1988). Adsorción física de gases y vapores por carbones . Universidad de Alicante. 465 p. ISBN: 84-86809-33-9. Edita: Secretariado de Publicaciones de la Universidad de Alicante. Alicante, España.

Menéndez, J. A. (1998). On the use of calorimetric techniques for the characterization of carbons: A brief review. *Thermochim. Acta*, Vol. 312, No. 1, pp. 79 – 86.

Molina-Sabio, M., Nakagawa, Y., Rodríguez-Reinoso, F. (2008). Possible errors in microporosity in chemically activated carbon deduced from immersion calorimetry. *Carbon,* Vol. 46, No. 1, pp. 329-334.

Montes-Morán, M.A., Suárez, D., Menéndez, J.A., Fuente, E.(2004) On the nature of basic sites on carbon surfaces: an overview. *Carbon*. Vol. 42*, No. 7*, pp.1219-*1225.*

Moreno, J. C. & Giraldo, L. (2005). Setups for simultaneous measurement of isotherms and adsorption heats. *Rev. Sci. Instrum.* Vol. 76, No. 1, pp. 1-8.

Moreno, J. C. (1996). Microcalorímetro de conducción de calor: diseño, construcción, calibración y su aplicación al estudio de sólidos porosos. Tesis doctoral, Universidad Nacional de Colombia, Bogotá,Colombia.

Moreno, J.C., Gómez, R., Giraldo, L. (2010). Removal of Mn, Fe, Ni and Cu Ions from Wastewater Using Cow Bone Charcoal, *Materials*, Vol. 3, pp. 452-466.

Moreno-Castilla, C., López-Ramos, M..V. (2007). Adsorción de compuestos organicos disueltos en agua sobre carbones activados. En: Sólidos Porosos: preparación, caracterización y aplicaciones, Ediciones Uniandes, Editor académico, Juan Carlos Moreno-Piraján, ISBN 978-958-695-276-7, Bogotá, Colombia, pp. 281-299.

Moreno-Castilla, C., Álvarez-Merino, M.A., Pastrana-Martínez, L.M., López-Ramón, M.V. (2010) Adsorption mechanisms of metal cations from water on an oxidized carbon surface. *Journal of Colloid and Interface Science*. Vol. 345, *No. 2*, pp. 461-*466.*

Moreno-Piraján, J. C. & Giraldo, L. (2007). Instrumentación calorimétrica aplicada a la determinación de entalpías de inmersión de sólidos porosos. En: Sólidos Porosos: preparación, caracterización y aplicaciones, Ediciones Uniandes, Editor académico, Juan Carlos Moreno-Piraján, ISBN 978-958-695-276-7, Bogotá, Colombia, pp. 281-299.

Moreno-Piraján, J.C., Navarrete, L., Giraldo, L., García, V. (2007). Adsorption of Phenol and 3 Chlorophenol on Activated Carbons using Immersion Calorimetry, *Información Tecnológica*, Vol. 18 , No. 3, pp. 71-80.

Nadhem, K. H., Xiao, D. C., Mohammed, M. F. (2001). Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust. *Chemical Engineering Journal*, Vol 84, pp. 95-105.

Nakagawa, Y., Molina-Sabio, M., Rodríguez-Reinoso, F. (2007). Modification of the porous structure along the preparation of activated carbon monoliths with H_3PO_4 and $ZnCl_2$.*Micropor. Mesopor. Mat*. Vol. 103, No. 1-3, pp. 29-34.

Oke, I.A., Olarinoye, N.O., Adewusi, S.R.A. (2008). Adsorption kinetics for arsenic removal from aqueous solutions by untreated powdered eggshell. *Adsorption*, Vol. 14, pp. 73-83.

Petit, C., Peterson, G.W., Mahle, J., Bandosz, T.J. (2010) The effect of oxidation on the surface chemistry of sulfur-containing carbons and their arsine adsorption capacity. *Carbon.Vol.48,No. 6*,pp. 1779-*1787.*

Puziy, A.M., Poddubnaya, O.I., Martínez-Alonso, A., Suárez-García, F., Tascón, J.M.D. (2002) Synthetic carbons activated with phosphoric acid: I. Surface chemistry and ion binding properties.*Carbon*. Vol.40*, No.9*, pp.1493-*1505.*

Radovic, L.R., Moreno-Castilla, C., Rivera-Utrilla, J. .(2000) Carbon Materials as Adsorbents in Aqueous Solutions. In *Chemistry and Physics of Carbon.* A Serie of Advances. Ed Marcel DekkerNew York. p 293-297

Rivera-Utrilla, J., Sánchez-Polo, M. (2003) Adsorption of Cr(III) on ozonised activated carbon. Importance of Cπ—cation interactions. *Water Research*. Vol. 37*, No. 14*, pp. 3335-*3340.*

Rodríguez, F. J. (2003). Procesos de potabilización del agua e influencia del tratamiento de ozonización, Ediciones Díaz de Santos S.A, ISBN 978-84-7978-587-1, Madrid, España.

Rodríguez-Reinoso, F. (2007). El carbón activado como adsorbente universal. En: Sólidos Porosos: preparación, caracterización y aplicaciones, Ediciones Uniandes, Editor académico, Juan Carlos Moreno Piraján, ISBN 978-958-695-276-7, Bogotá, Colombia, pp.1-42.

Rodriguez-Reinoso, F., Almansa, C., Molina-Sabio, M. (2004). Adsorption of methane into $ZnCl_2$ activated carbon derived disc. *Micropor. Mesopor. Mat*, Vol. 76, No. 1-3, pp. 185-191.

Rouquerol, F., Rouquerol, J., Sing, K. S. W. (1999). Adsorption powders and porous solids Principles, methods and applications, Academic Press, 1st edition, ISBN 0125989202, San Diego, London.

Ruthven, D. M. (1984). Principles of Adsorption and Adsorption Processes, Wiley - Interscience, ISBN 0471866067, New York, United States.

Silvestre-Albero A., Silvestre-Albero J., Sepúlveda-Escribano A., Rodríguez-Reinoso, F. (2009) Ethanol removal using activated carbon: Effect of porous structure and surface chemistry. *Microporous and Mesoporous Materials*. Vol.120*, No. 1-2*, pp. *62-68*.

Silvestre-Albero, J., Gómez de Salazar, C., Sepulveda-Escribano, A., Rodríguez-Reinoso, F. (2001). Characterization of microporous solids by immersion calorimetry. *Colloid and Surfaces A: Physicochem and Eng Aspect,* Vol. 187–188, pp.151–165.

Smiciklas, I., Dimovic, S., Sljivic, M., Plecas, I. (2008). The batch study of Sr^{2+} sorption by bone char, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng*., Vol. **43, No.** 2, pp. 210-217.

Stoeckli, F., Ballerini, L., De Bernardini, S. (1989). On the evolution of micropore widths and areas in the course of activation. *Carbon*, Vol. 27, No. 3 , pp. 501-502.

Stoeckli, F., Moreno-Castilla, C., Carrasco-Marín, F., Lopez-Ramón, M.V. (2001) Distribution of surface oxygen complexes on activated carbons from immersion calorimetry, titration and temperature programmed desorption techniques . *Carbon*.Vol 39*, No. 14*, pp.2235-*2237.*

Stoekli, H. F. & Kraehenbüehl F. (1989). Recent developments in the Dubinin equation. *Carbon*, Vol. 27, No.1, pp. 125-128

Su-Hsia, L. & Ruey-Shin, J. (2009). Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review. *J. Environ. Manag*., Vol. 90, No. 3, pp. 1336–1349.

Szymański, G., Biniak, S., Rychlicki . G. (2002) Carbon surface polarity from immersion calorimetry. Fuel processing Technology.*Vol.79* , pp. *217-223*

Szymański, G., Karpiński, Z., Biniak S., Świątkowski, A. (2002) The effect of the gradual thermal decomposition of surface oxygen species on the chemical and catalytic properties of oxidized activated carbon. *Carbon*. Vol.40*, No.14*, pp.2627-*2639*

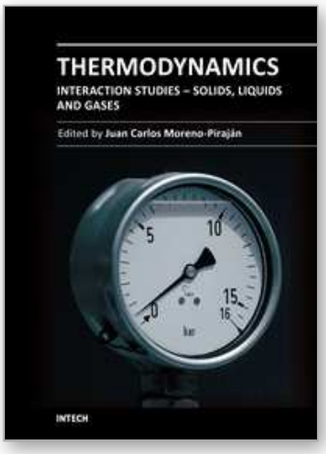
Tae Young, K., Seung Jai, K., Sung Young, C. (2001). Effect of pH on Adsorption of 2,4-Dinitrophenol onto an Activated Carbon. *Korean J. Chem. Eng*., Vol.18, No. 5, pp. 755-760.

Vargas, D.P., Giraldo, L., Moreno-Piraján, J.C. (2010). Preparation and Characterization of Activated Carbon Monoliths with Potential Application as Phenol Adsorbents., *E-J. Chem*. No. 7, pp. 531-539.

Yang, R. T. (1997). Gas Separation by Adsorption Processes, Imperial College Press, Butterworth, ISBN 9780471297413, London, UK.

Yin, C.Y., Aroua, M.K.., Daud, W. (2007) Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions *Separation and Purification Technology*. Vol 52*, No.3*, pp.403 *415.*

Zimmermann, W. & Keller, J. U. (2003). A new calorimeter for simultaneous measurement of isotherms and heats of adsorption. *Thermochim. Acta*, Vol. 403, No. 1, pp. 31 – 41.



Thermodynamics - Interaction Studies - Solids, Liquids and Gases
Edited by Dr. Juan Carlos Moreno PirajÃ¡n

ISBN 978-953-307-563-1
Hard cover, 918 pages
Publisher InTech
Published online 02, November, 2011
Published in print edition November, 2011

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