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Calorimetry of Immersion in the Energetic Characterization of Porous Solids

Liliana Giraldo, Paola Rodríguez-Estupiñán and Juan Carlos Moreno-Piraján

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Abstract

In order to study and understand the adsorption process in a liquid-solid interface, it is necessary to know both textural and chemical properties of the adsorbent. It is also important to know the behavior of the solid in a liquid medium, considering that the interaction can produce some changes in the texture and the electrochemical properties when the adsorbent is immersed in a solvent or a solution. The study of the influence of these properties in the adsorption process with techniques like immersion microcalorimetry can provide direct information on particular liquid–solid interactions. The parameter that is evaluated by immersion microcalorimetry is the immersion enthalpy, ΔH_{im} . Immersion enthalpy is defined as the energy change at temperature and pressure constants when the surface of the solid is completely immersed in a wetting liquid in which the solid is insoluble and does not react. The immersion calorimetry can be a versatile, sensitive and precise technique that has many advantages for the characterization of porous solids. The versatility of immersion microcalorimetry is because changes in surface area, surface chemistry, or microporosity will result in a change in immersion energy. The interactions solid-liquid can be physical or chemical type, the physical present a lower amount of energy than that generated when exist chemical interactions.

Keywords: calorimetry, calorimeters type, immersion enthalpy, solids characterization, energetic change

1. Introduction

The calorimetric technique has been used in the last decades in the areas of thermodynamics, solutions, materials, biochemistry and biology, not only to obtain important thermodynamic parameters such as the enthalpy, ΔH , and the heat capacity, C_p , of the considered processes.

The calorimetry is a useful analytical tool, in the case of complex substrates such as those involved in the cited areas [1]. As many of these studies carried out in solution, it is interesting to know the interactions of different solutes with the solvent and in this way extend the results obtained to systems that are more complex. Then, it is interesting to analyze the calorimetric works in which water acts as a solvent, and the study of the interactions of this with the various solutes.

The transfer of energy in the form of heat is involved in all natural processes and this arouses interest in its quantitative determination. Cavendish built the first calorimeter in 1720 to determine the heat of vaporization of water and specific heats of various substances. Its appearance is the beginning of a great variety of designs of calorimetric equipment, which realized by the most important researchers of that time like Lavoisier, LaPlace, Black and Irvine, Bunsen, Dulong and Petit, Eucken and Nernst among others [2].

Due to the large number of systems, processes and conditions of interest, there is no single calorimeter model, so the diversity of these is very wide. Since the very emergence of calorimeters, a variety of equipment has been generated.

Parallel with the development of calorimeters, it was necessary to improve data capture systems, which led to the production of peripheral systems of high sensitivity and precision. With the development of the peripheral equipment, calorimeters were designed whose basic characteristic was the detection of small amounts of energy, which were called microcalorimeters [3].

The purposes and applications of calorimeters have broadened the field of study and concepts of calorimetry, and therefore of thermodynamics: the enthalpies of solution, combustion, mixing and vaporization are just some of the determinations that performed with this technique. In modern calorimetry, instruments have been developed to allow studies in biological systems, in what has been called BioCalorimetry. It is possible to measure and advance in the field of knowledge, in subjects such as thermally induced transitions in proteins, lipids, nucleic acids, determination of heat production by living cells and microorganisms [4]. Calorimetric measurements have special validity in this subdiscipline.

Calorimetry is used in so-called Surface Science, with which it can have access to the chemistry itself and the interactions of the molecules that are exposed to the surface. The composition of the surface at the atomic level can be defined by instrumental methods including X-ray techniques, infrared spectroscopy, NMR, among others; however, the characterization of surface chemistry of the solids finds in microcalorimetry a valuable technique. Processes such as adsorption, desorption, immersion, solubilization or solvation, mixing, chelation and others can follow and interpret by means of calorimetric techniques, directly and without too much cost. Certain fields have advanced so autonomously that they have a proper name like Immersion Calorimetry.

Leslie [5] in 1802 directs his research to the determination of surface areas whose results have led to develop versatile methods for the characterization of porous solids, especially in activated carbons, with the possibility of obtaining very precise information of polarity, hydrophobicity, active sites and other properties [6–8]. It is also possible to establish

relationships between the thermal pretreatment to which the porous solids are exposed with the enthalpy of immersion [9, 10], as well as being a useful tool in the characterization of functional groups.

The immersion calorimetry is based mainly on the models developed by Dubinin [11] in Russia and Stoekli and Kraehnuehl [12] in Switzerland, with which it is possible to determine the total area of activated carbons and other solids.

A description of the type of calorimetric instrumentation used in the characterization of porous solids will be made, the most important relationships for the description of the surface of the solids by means of enthalpic determinations will be established, and some applications of the determination of the enthalpies of immersion as a solid characterization parameter will be shown.

2. The calorimetric technique

Calorimetry is a technique of thermodynamic character that allows knowing the amount of energy that is transferred as heat in a certain process and is related to the energy content of the studied system. The determination of the amount of energy absorbed or produced by a system has been carried out for several centuries, so that the calorimetry is one of the oldest measurement procedures, which is associated with the change of a system [13].

With the increase in sensitivity and precision of the methods for measuring small amounts of energy, in the order of 10–100 mJ, such as those produced in the solid-gas and solid-liquid interaction the calorimetric techniques used with higher frequency. Calorimetry used too in different fields since they supply information complementary to the extensive studies of gas-phase adsorption isotherms (vapor) and in liquid phase.

Due to the wide number of systems, processes and conditions does not exist a unique calorimeter model. The calorimeters diversity is wide and its classification depends on different factors like: the form in which the measurement is carried out and the type of sensors that are used, the change that takes place in the calorimetric cell, the way in which the energy transport is performed and the system-surroundings operating conditions.

Taking into account the surrounding system operating condition, the calorimeters are classified commonly in adiabatic calorimeters, isoperibolic calorimeters, isothermal calorimeters and differential scanning calorimeters [14]. The aspects to be taken into account to perform the calorimetric determination are: the required precision, the working temperature, the amount of sample available, the magnitude of the energy involved, the duration of the experiment and the cost of the instrument.

2.1. Adiabatic calorimeter

Ideally, adiabatic calorimeters do not allow heat exchange between the cell and the surroundings. Three ways can be considered to achieve this goal:

1. When the heat generation is so fast, no appreciable amount can enter or leave the cell during the period in which the measurement is carried out.
2. In the case of separating the cell from the surroundings with a thermal resistance, R_T , infinitely large, so that the measuring system is as isolated as possible.
3. By means of external electronic controls that make the surrounding temperature as close as possible to that of the cell.

During the calorimetric experience, any heat generated or consumed in the cell lead to a temperature change, which is evaluated from a plot of temperature as a function of time. The heat can be calculated from the measurement of the temperature difference ΔT :

$$Q = Cp\Delta T \quad (1)$$

The heat capacity is easily determined by calibration with the use of electrical energy [15].

2.2. Isoperibolic calorimeter

An isoperibolic calorimeter keeps constant the surrounding temperature by using a thermostat, while the temperature of the measuring system may vary over time. There is a thermal resistance, R_T , of magnitude defined between the surroundings and the cell where the measurement is made, so that the heat exchange depends on its temperature difference.

T_A is the surrounding temperature and T_C is the cell temperature and measurement system. Since T_A is constant then the heat flux is a C_T function.

The decrease in T_C depends on the insulation of the cell that defines the thermal leakage constant, K_{ft} , calorimeter's parameter and also a function of the temperature gradient.

The amount of heat for the process under consideration is equal to:

$$Q = Cp \Delta T_{corrected} \quad (2)$$

where Cp is the heat capacity of the studied system plus the heat capacity of the cell, $\Delta T_{corrected}$ is the temperature difference on which a correction is made for small but existing heat leaks [16].

2.3. Isothermal calorimeter

Another way of performing the measurement of the energy involved in a process is in which there is a large exchange of heat that is produced in the cell with the surroundings; this is an isothermal nature method, in which the surroundings and the cell have the same constant temperature ($T_A = T_C = \text{constant}$).

The isothermal calorimeter has a small thermal resistance R_T and the heat capacity of the surroundings is infinitely large. If these requirements are taken into account, in strictly

isothermal conditions, T_A and T_C can remain constant in time and space, but then no heat flow occurs. In real cases, there is a heat flow between the cell and the surroundings, a flow that is detected by means of the thermal sensors placed between them. The flow is due to the generally small temperature difference between T_A and T_C during the occurrence of the observed process; the magnitude of this temperature difference depends on the amount of heat released per unit time, the thermal conductivities, the cell geometry and the type of insulation that the thermal sensors possess. In spite of these limitations, the isothermal designation is commonly used for calorimeters where the temperatures T_A and T_C may be different from each other, but each of them considered separately is constant throughout the time of occurrence of the process that generates the heat flow [17]. In **Figure 1**, a temperature curve as a function of time obtained with an isothermal calorimeter is presented, the conduction of heat to the surroundings is observed by the drop in temperature after the supply of a heat pulse to the cell.

The cell is connected to the surroundings by means of a thermal resistance R_T which is an interesting parameter because it relates the heat flow dQ/dt to the temperature difference. The temperature difference in the thermal resistance is:

$$\Delta T = T_c - T_A \quad (3)$$

and in the steady state this relation is presented:

$$\frac{dQ}{dT} = \frac{\Delta T}{R_T} \quad (4)$$

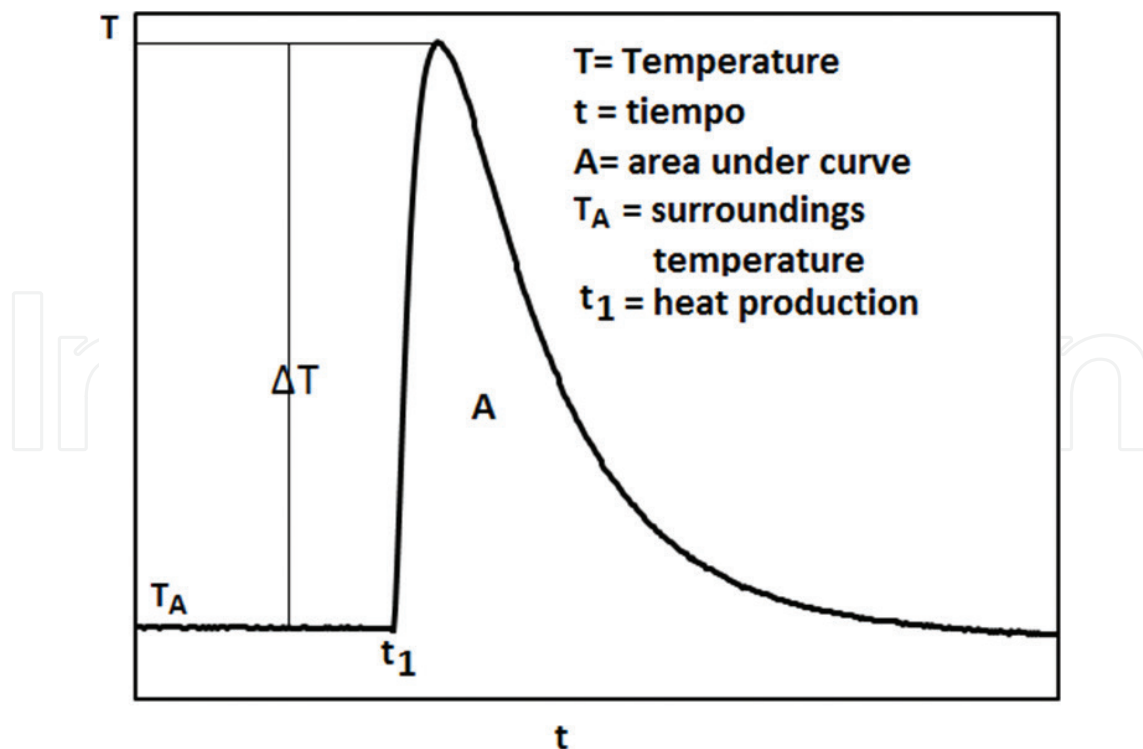


Figure 1. Temperature curve as a function of time for an isothermal calorimeter.

integrating Eq. (4) is obtained:

$$Q = \frac{1}{R_T} \int \Delta T(t) dt \quad (5)$$

For the same amount of heat:

$$\int \frac{\Delta T(t) dt}{R_T} = \text{constant} \quad (6)$$

Due to the complex nature of the heat conduction within a real instrument, it is generally impossible to calculate the R_T resistance, which quantitatively connects the measured temperature difference with the corresponding heat flow; for this reason, the resistance must be determined by calibration. The reciprocal value of the thermal resistance is the calibration factor K (t)

$$Q = K \int \Delta T(t) dt \quad (7)$$

In many cases, the calibration factor K can record as constant in the temperature range in which carry out the process.

2.4. Temperature scanning calorimeter

In this type of calorimeter, a constant temperature change of the surroundings is carried out which is reflected in the measuring cell with a certain delay that depends on the magnitude of the thermal resistance R_T between the system and the surroundings.

The surrounding temperature will be equal to:

$$T_s = T_{s_{init}} + \beta t \quad (8)$$

where T_s and $T_{s_{init}}$ are the surrounding temperature and the initial surrounding temperature respectively, β is the rate of change in temperature and t is the time. This form of operation is the one used in differential scanning calorimeters [18].

3. Application of the enthalpy of immersion in the characterization of activated carbon

The work that shown below uses an isothermal heat conduction calorimeter with thermopiles as heat flux sensors and measures the interaction energy that occurs when activated carbon immersed in water and in aqueous solutions of Cd (II) and Ni (II) [19].

3.1. Relationship between the enthalpy of immersion and the porous solid surface

The immersion calorimetry is a technique of thermodynamic character that allows to evaluate the thermal effects that result to put in contact a solid with a liquid and thus to know the heat involved in the interactions that are established and express it like the enthalpy of immersion ΔH_{im} . [20]. The interactions may be of specific or non-specific type and the magnitude of the heat generated depends on the intensity of the interaction [21].

The thermal effects resulting from immerse a solid in a non-polar solvent such as benzene are related to the formation of a layer of molecules on the solid and therefore with surface parameters, as shown by the model developed by Dubinin and Stoeckli, that for a microporous solid, defines the enthalpy of immersion as [22]:

$$\Delta H_{im}(T) = \int_0^1 q^{ne}(T, \theta) d\theta \quad (9)$$

where q^{net} is the heat of adsorption.

Stoeckli established the relationship between the enthalpy of immersion of activated carbon in various organic liquids and the parameters obtained by the adsorption of vapors of the same liquids on the solid. This relation is described by the equation of Stoeckli and Krahenbuehl [23]:

$$-\Delta H_{im} = \frac{\beta E_o W_o \sqrt{\pi}(1 + \alpha T)}{2V_m} \quad (10)$$

where β is the affinity coefficient of the adsorbate, E_o is the characteristic free energy for the adsorption of the reference vapor, W_o is the total volume of micropores of the solid, α is the thermal expansion coefficient of the adsorbate at temperature T and V_m is the molar volume of the liquid.

When the above equation is applied directly to activated carbons, which have a small external surface, the experimental enthalpy, ΔH_{exp} , also contains a contribution due to the external surface (S_{ext}).

$$\Delta H_{exp} = \Delta H_{im} + h_i S_{ext} \quad (11)$$

where h_i is the specific immersion enthalpy to non-porous open surface. From the above equation, the total area can be calculated as:

$$A_{Total} = A_{microp} + S_{ext} \quad (12)$$

Stoeckli et al. use this technique to characterize the porous structure of a wide variety of carbonaceous materials taking a non-porous carbon black as a reference, assuming that the immersion enthalpy per surface area is proportional to the available surface to the immersion liquid [24].

The immersion enthalpy of a solid in different liquids is usually different, therefore the magnitude of the immersion enthalpy will depend on [25]:

1. The extent of the surface area of the solid, thus for a solid–liquid system, the immersion energy is increased with the surface area of the solid. If calorimetry of immersion is performed with liquids of different molecular size but similar chemical nature, it is possible to obtain an approximation to pore size distribution.
2. The chemical nature of the surface and the immersion liquid: if the liquid is polar the immersion energy increases with the polarity of the chemical functions on the surface of the solid. This information is useful to evaluate the influence of modification treatments of the surface chemistry, such as oxidation and heat treatments, the polarity and the hydrophobic character of the surface.

Water immersion calorimetry allows evaluate the polarity of the activated carbon surface under the assumption that water molecules interact mainly with the oxygenated surface groups located at the polar sites at the edges of the graphene layers [26]. It has even been found that the enthalpy of immersion increases linearly with the concentration of the acidic sites present on the surface of the solid [27].

3.2. Application: Activated carbons modified in their surface chemistry. Immersion in water and aqueous solutions of Cd (II) and Ni (II)

A granular activated carbon prepared from coconut shell (CAG), is modified in its surface chemistry to obtain seven solids with different characteristics. Immersion enthalpies in water and aqueous solutions of Ni (II) and Cd (II) were determined, this with the purpose of establishing the differences in the energetic interactions of the solids with the liquids and the influence that shows the superficial chemistry of the activated carbons in the values of the enthalpies of immersion.

3.2.1. Materials and methods

A series of activated carbons are obtained of a granular activated carbon prepared from coconut shell (CAG) which is oxidized with a solution of 6 M nitric acid (CAGoxN) and 10 M hydrogen peroxide (CAGoxP). Two portions of each oxidized activated carbon were treated at 450°C (CAGoxN450 and CAGoxP450) and 750°C (CAGoxN750 and CAGoxP750) under nitrogen atmosphere and a final activated carbon was obtained by heating the starting activated carbon at 900°C (CAG900) [28].

3.2.1.1. Textural characterization

Textural parameters of surface area and pore volume of the activated carbons evaluate by physical adsorption of N₂ at -196°C and CO₂ at 0°C in an Autosorb 3B automatic equipment, Quantachrome. The apparent surface area and the micropores volume determine by the Brunauer-Emmet-Teller (BET) and Dubinin-Radushkevich models respectively.

3.2.1.2. Chemical characterization

3.2.1.2.1. Total acidity and basicity

The total acidity and basicity of the activated carbons evaluate by the Boehm method [29]. 1000 g of each sample weighed and 50 mL of a 0.1 M NaOH solution was added to determine the acidity, or 50 mL of a 0.1 M HCl solution to determine the basicity, considering that in each mixture the acid and basic groups present on the surface of the activated carbon are neutralized. The mixtures maintained at a temperature of 298 K and constant agitation for 5 days, at the end of this equilibrium time taken a 10 mL aliquot of each supernatant liquid and titrated with a previously standardized NaOH or HCl solution, as appropriate.

3.2.1.2.2. Point of zero charge

The determination of the pH at the point of zero charge, pH_{pZC} , evaluated by the mass titration method [30], by weighing different amounts of activated carbon between 10 and 600 mg,

placed in glass containers with 10 mL of a 0.1 M solution of NaCl. The mixtures were maintained at 298 K and constant stirring for 2 days. The pH of each solution was then measured with a Schott pH 840B pH meter.

3.2.1.2.3. Determination of immersion enthalpies

The enthalpies of immersion of the activated carbons in water and aqueous solutions of Ni (II) and Cd (II) of 500 mg L⁻¹ were determined in a heat conduction microcalorimeter that has thermopile as heat flow sensors and a cell in stainless steel with a capacity of 15 mL, in which 10 mL of the immersion liquid is placed.

Weighed 100 mg of each activated carbon in a glass ampoule fitted in the calorimeter cell and captured the electric potential of the thermopiles for about 40 minutes until obtained a stable baseline. Then the immersion of the sample is performed recording the potential increase caused by the wetting of the solid, it is waited until it is returned to the baseline and the electrical calibration is carried out [31].

3.2.2. Results and discussion

Table 1 shows the results obtained for the textural characterization of the obtained carbons, which indicates the changes that occur in these characteristics by the chemical and thermal treatments that were made to the solids.

The results presented are: the surface area calculated by the BET model, the micropore volume (W_o) estimated by the DR model and the mesopore volume (V_{meso}). The narrow microporosity (V_n) of the materials was evaluated by applying the DR model to the experimental data obtained from the CO₂ adsorption isotherm.

The results obtained show that the activated carbon exposed to the oxidation treatment with nitric acid, CAGoxN, presents a decrease in the surface area and in the micropore volume (W_o), with respect to the starting activated carbon. This behavior is due to the treatment of oxidation, which favors the formation of oxygenated surface groups that are located at the edges of pore apertures, which limits the accessibility of the nitrogen molecule to porous structures [32].

Activated carbon	N ₂		CO ₂	
	Surface area BET (m ² g ⁻¹)	V _o (cm ³ g ⁻¹)	V _{Meso} (cm ³ g ⁻¹)	V _n (cm ³ g ⁻¹)
CAG	842	0.34	0.04	0.35
CAG900	876	0.35	0.05	0.28
CAGoxN	816	0.32	0.05	0.38
CAGoxN450	903	0.35	0.05	0.37
CAGoxN750	935	0.37	0.05	0.35
CAGoxP	873	0.35	0.04	0.36
CAGoxP450	783	0.31	0.03	0.32
CAGoxP750	888	0.35	0.04	0.34

Table 1. Textural characteristics of the activated carbons determined from the N₂ and CO₂ isotherms at -196 and 0°C.

According to studies reported the groups developed are acid carboxylic and carbonyl type, besides in the solids modification with solutions of HNO_3 occurs the collapse of porous structures, this latter effect explains the increase in the mesoporosity volume.

In the oxidized activated carbon with hydrogen peroxide, an increase in the surface area near 7.0% with respect to the sample CAG is observed, since in addition to the process of oxygenated surface formation there is also the opening of porous structures [33].

The thermal treatments on the activated carbon, which produce the decomposition of oxygenated groups, show changes in the surface area values, an increase for the CAGoxN sample a decrease for CAGoxP, and an increase for the higher temperature.

Table 2 presents the results obtained for total acidity and basicity and for pH at the point of zero charge, which reflects the changes that occur in the surface of the activated carbon with the different processes.

Oxidation with HNO_3 and H_2O_2 solutions produces the formation of surface functional groups, with regard to the oxidation process with nitric acid is more effective in the formation of acid groups on the surface of the activated carbon [34], the increase of these groups is close to triple, with respect to the original sample. Hydrogen peroxide has a smaller effect on the reduction of the basic character of the surface, this leads to an increase in pH_{pZC} which is 6.2 for the CAGoxP sample.

Once the activated carbon is characterized, the immersion calorimetry is carried out in order to obtain the enthalpies of immersion, ΔH_{im} , of the activated carbon in water. This solvent interacts with the surface oxygenated groups of the solids and it has wanted to show how the differences obtained in the surface chemistry of the solids are reflected in the thermal curves of electric potential as a function of time for each set of activated carbons. **Figure 2** shows the thermal curves obtained for the immersion of CAG and CAG900 activated carbons in water.

As the area under the potential as a function of time curve is proportional to the heat generated in the immersion of the solid in the liquid. It is observed that the activated carbon

Activated carbon	Total acidity (molecules/nm ²)	Total basicity (molecules/nm ²)	pH _{pZC}
CAG	0.141	0.065	5.4
CAG900	0.032	0.191	8.9
CAGoxN	0.290	0.036	3.4
CAGoxN450	0.179	0.069	7.9
CAGoxN750	0.039	0.172	8.2
CAGoxP	0.204	0.073	6.2
CAGoxP450	0.126	0.197	7.2
CAGoxP750	0.058	0.201	8.7

Table 2. Chemical characterization of activated carbons.

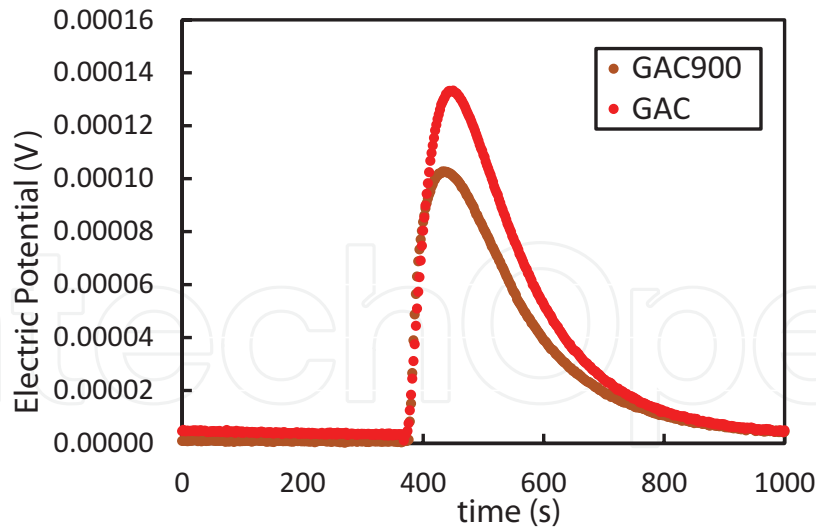


Figure 2. Thermal curves of the immersion of CAG and CAG900 activated carbons in water.

CAG900, that has been exposed to a thermal process at 900°C in which a large part of the surface groups are removed and with respect to the starting carbon shows an increase in pH_{PZC} exhibits a smaller peak because the interactions of the water with the surface of this activated carbon decrease.

In immersion calorimetry, benzene is the reference solvent because its affinity coefficient, β , is defined as 1. The benzene to be a non-polar solvent presents different energetic behavior with activated carbons compared to water, by showing a greater interaction with the activated carbon that has a lower content of surface oxygenated groups and a smaller interaction with the solids that have been oxidized. **Figure 3** presents the curves obtained for the immersion of activated carbon CAG900 and CAGoxN in benzene.

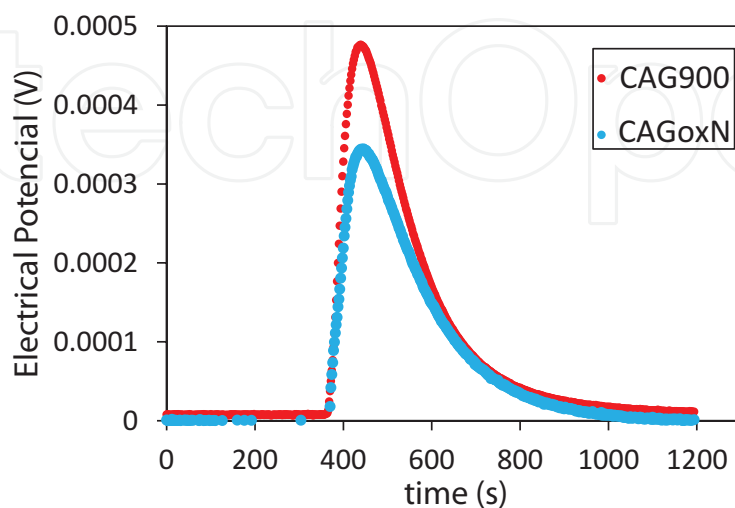


Figure 3. Thermal curves of the immersion of CAG900 and CAGoxN activated carbons in benzene.

Figure 4 shows the electrical potential as a function of time curves obtained when CAGoxN, CAGoxN450 and CAGoxN750 are immersed in water. This Figure show the following trend: the highest peak occurs for activated carbon oxidized with nitric acid, which has the uppermost content of oxygen groups and therefore the highest interaction with water and provides information of the energy manifested between the surface and the polar molecules of water.

Oxidized activated carbons with nitric acid solution and subsequently exposed to thermal treatments selectively lose oxygenated groups, as is known by some works about surface chemistry of activated carbons [35], and therefore the interactions with water are smaller as may be observed in thermograms.

In **Figure 5**, present the themal curves for the other group of activated carbons oxidized. These solids were oxidized with hydrogen peroxide solution and heat treatment at 450 and 750°C.

The result obtained is comparable, in the trend, to the previous one since the oxidized activated carbon shows the highest interaction and it's followed by the activated carbon treated at the intermediate temperature and finally the lowest effect is obtained for the sample being treated at the highest temperature.

Observe that the group of activated carbons oxidized with HNO_3 solution present greater effects than those oxidized with H_2O_2 solution and it makes a difference in how the oxygenated groups are generated on the surface of the activated carbon.

The activated carbons obtained are used for the adsorption of Ni (II) and Cd (II) ions from aqueous solution, the ions adsorption on the surface of the activated carbons also produces a thermal effect that can be evaluated by calorimetry. Calorimetry allows calculating the total amount of heat generated in the process. For case of the activated carbon immersion in the aqueous solutions of the ions, the thermal effect obtained corresponds to the summation of several interactions as the wetting of the surface by the solvent, the solvent the interaction

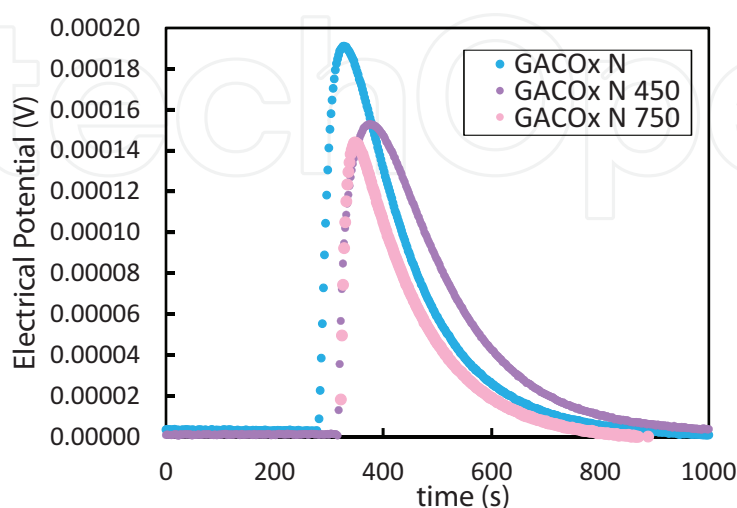


Figure 4. Thermal curves of the immersion in water of activated carbons of the oxidized series with nitric acid solution.

with the chemical groups of the surface, the interaction of the ions with the surface and their groups, among others.

Figure 6 shows the thermal curves obtained for the immersion of the activated carbon in aqueous solutions of Ni (II) ion, for the solids with the lowest and the highest adsorption of the ion. The CAGoxN activated carbon has a higher peak in the potential curve as a function of time when it is brought into contact with the 500 mg L⁻¹ solution, indicating that the ion present in the liquid produces a greater thermal effect. This effect relates to the interaction of the ions with the oxygenated groups of the surface, since in the immersion of the activated carbon CAG900 in which diminished the content of surface groups, the thermal effect is considerably smaller.

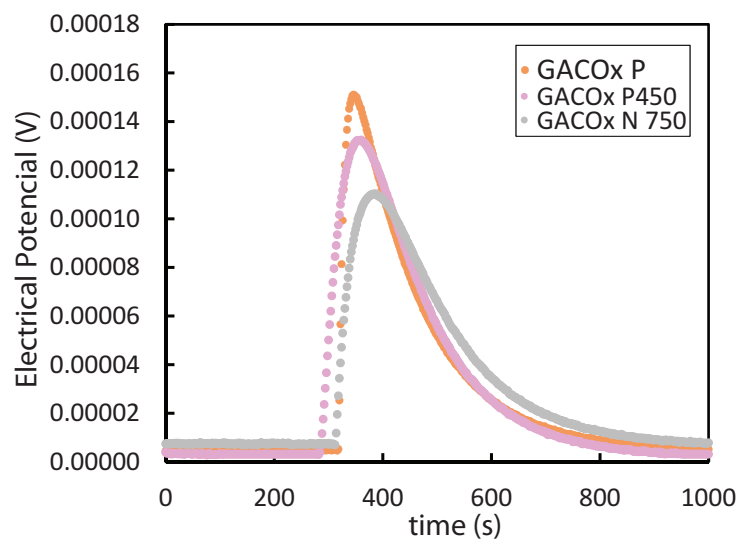


Figure 5. Thermal curves for the immersion of the activated carbon group oxidized with hydrogen peroxide solution in water.

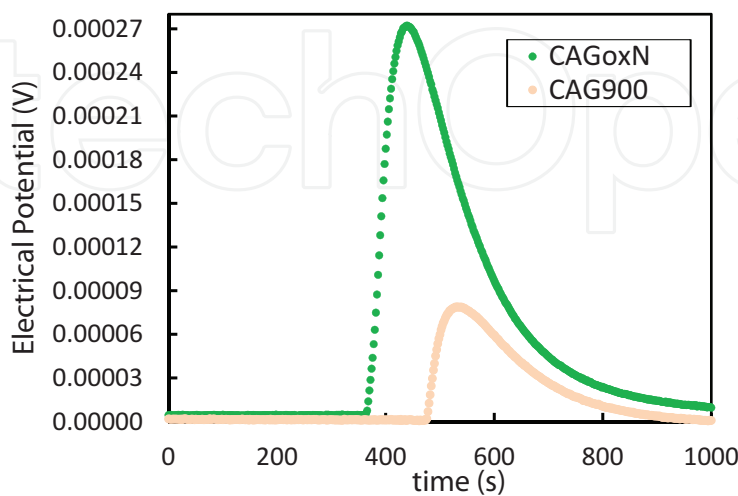


Figure 6. Thermal curves for the immersion of the activated carbon CAG900 and CAGoxN in aqueous solution of 500 mg L⁻¹ of Ni (II).

Figure 7 shows the thermal curves obtained for the immersion of the CAGoxP and CAG900 activated carbons in a solution of 500 mg L^{-1} of Cd (II), for these activated carbons the highest and lowest adsorption of the Cd (II) ion are obtained, respectively. For the immersion of CAGoxP, a larger peak is observed indicating that there is a greater effect between the solid and the solution, and that the surface chemistry of activated carbon has an influence on the generation of a quantity of heat produced by the interaction between them.

Once the immersion calorimetry of the different activated carbons into the described immersion liquids is carried out, the enthalpies of immersion are calculated. The results present in **Table 3**, which shows the enthalpies in water and aqueous solutions of 500 mg L^{-1} of Ni (II) and Cd (II) for the original activated carbon, the reduced and the two oxidized activated carbons.

It is interesting to observe the values of the immersion enthalpies obtained, since they can be related to the change that was caused to the surface chemistry of the activated carbon. Because the two oxidizing agents and the interaction of the two ions with the surface is different, it

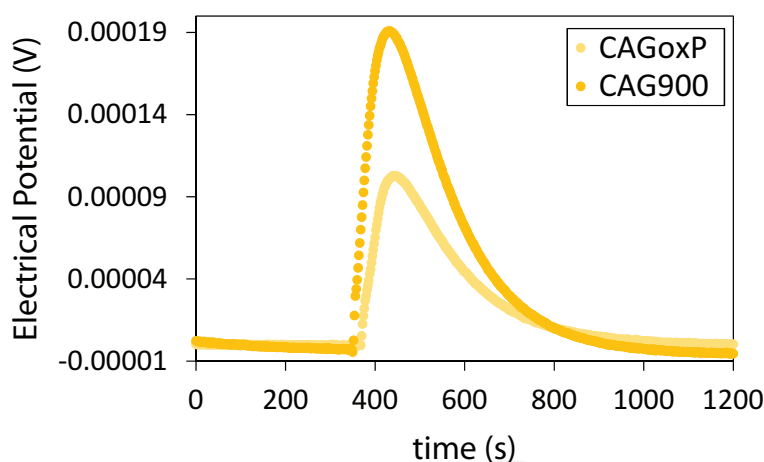


Figure 7. Thermal curves for the immersion of CAG900 and CAGoxN activated carbons in aqueous solution of 500 mg L^{-1} of Cd (II).

Activated carbon	$-\Delta H_{\text{im}}$ in H_2O (J g^{-1})	$-\Delta H_{\text{im}}$ in Ni (II) solution (J g^{-1})	$-\Delta H_{\text{im}}$ in Cd (II) solution (J g^{-1})
CAG	49.65	49.96	34.42
CAG900	32.39	37.50	34.40
CAGoxN	66.59	67.17	52.96
CAGoxP	56.42	45.64	57.73

Table 3. Enthalpies of immersion of activated carbons in different liquids.

opens the possibility of conducting studies between immersion enthalpies into the solutions of ions and contents of specific groups produced on the surface.

Immersion enthalpies can relate to the textural and chemical characteristics of the activated carbon. **Figure 8** shows the relationship between the enthalpy of immersion of activated carbons in benzene and the micropore volume, that is one of the frequent representations for these characterization parameters, and for microporous activated carbons is directly proportional [36].

Observe, as a general trend, that when the micropore volume increases the immersion enthalpy increases too. As made a modification on the surface chemistry of the solid, several of the activated carbons keep the micropore volume and the values obtained for the enthalpies of immersion of the activated carbons in benzene are consistent with the chemical changes that occur.

Can to say for the activated carbon CAG900 with a micropore volume of $0.35 \text{ cm}^3 \text{ g}^{-1}$ that the greater immersion enthalpy value is generated because this is the most hydrophobic solid. Then it will have a greater interaction with benzene, and the activated carbon CAGoxN450, which has the same micropore volume value has the lower value of enthalpy of immersion in benzene since it has a higher content of oxygenated groups.

Finally, the immersion enthalpies of the set of activated carbons in the non-polar solvent benzene, and the polar solvent water, with the pH of each solid at the point of zero charge are reported, which is shown in **Figure 9**.

It is observed that when pH_{PZC} increases, the immersion enthalpy in benzene increases because when the content of oxygenated groups decreases the basicity of the activated carbons increases as well as its hydrophobic character; in contrast, when the content of oxygenated groups increases, so does the acidity and the interactions with water manifested in the enthalpy of immersion.

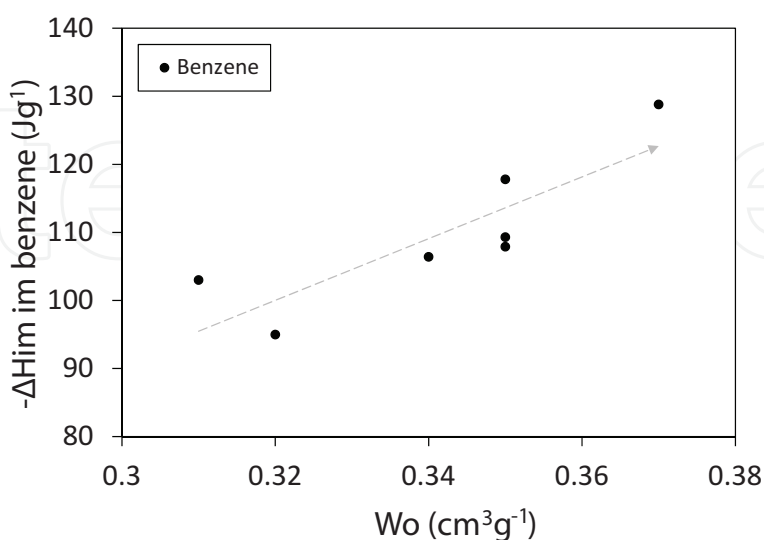


Figure 8. Enthalpy of immersion of the activated carbons in benzene as a function of the micropore volume.

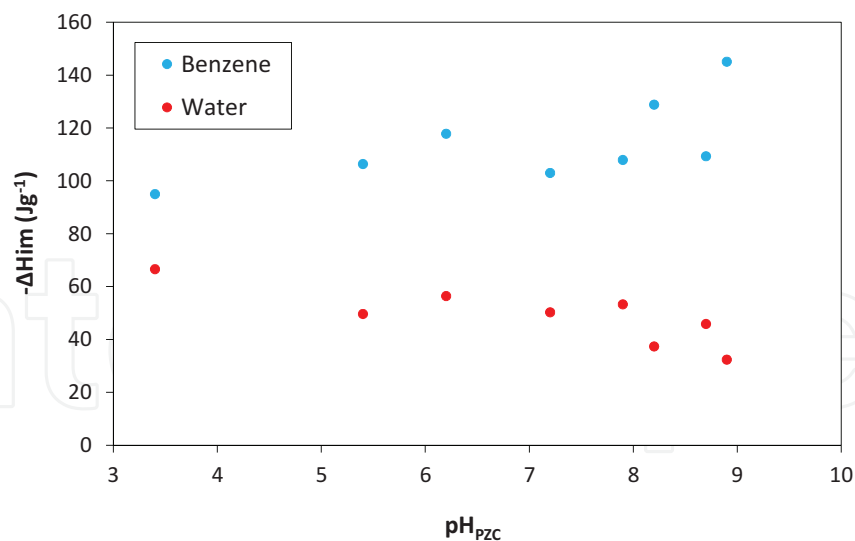


Figure 9. Enthalpy of immersion of activated carbons in benzene and water as a function of pH at the point of zero charge.

4. Conclusions

Activated carbons obtained from a granular activated carbon by oxidation of its surface with solutions of nitric acid and hydrogen peroxide and subsequent heat treatment, the solids obtained have surface areas between 783 and 935 m² g⁻¹.

The treatment with nitric acid mainly favors the formation of acidic groups, specifically carboxylic groups, obtaining a density of these groups of 0.197 molecules/nm². In addition, it causes a decrease in the parameter of basicity, in contrast, the treatment with hydrogen peroxide favors the formation of phenolic groups (0.075 molecules/nm²) and its effect on the decrease of the basicity parameter is smaller.

Modified the point of zero charge of the solids by the change in the concentration of the surface groups promoted by each treatment, a greater amount of acid groups as in the case of the sample GACoxN produces an acid pH_{PZC}, in this case 3.4.

The immersion enthalpies in water and the total acid and basic surface groups content present a relation and show that these values are influenced by the interactions of the oxygenated surface groups and basic groups free of oxygen.

The enthalpies of immersion of the activated carbons in the solutions of the electrolytes show that these enthalpies were larger for the GACoxN-Ni (II) and GACoxP-Cd (II) systems, evidencing the affinity and selectivity of the solids by the respective ions.

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Author details

Liliana Giraldo^{1*}, Paola Rodríguez-Estupiñán² and Juan Carlos Moreno-Piraján²

*Address all correspondence to: lgiraldogu@unal.edu.co

1 Faculty of Sciences, Department of Chemistry, Research Group on Porous Solids and Calorimetry, Andes University, Bogotá, Colombia

2 Faculty of Sciences, Department of Chemistry, National University of Colombia, Bogotá, Colombia

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