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# Enthalpic characterization of activated carbons obtained from *Mucuna Mutisiana* with different burn-offs

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**Abstract** Immersion enthalpies of activated carbon samples obtained by activation with steam at temperatures between 600 and 900 °C and activation times between 1 and 10 h were determined. The calorimetric liquids of immersion are $CCl_4$, water, NaOH, and HCl 2 M solutions, and the values of the immersion enthalpies are related to other properties of the activated carbons such as the surface area B.E.T., the micropore volume, the content of acid, and basic surface groups. The highest values for the immersion enthalpies take place for the polar solvent $CCl_4$ and for HCl solution, with values between 4.0 and 75.2 J g$^{-1}$ and 9.15 and 48.3 J g$^{-1}$, respectively.

**Keywords** Activated carbons · Immersion enthalpy · Surface area · Micropore volume · Chemical surface groups

## Introduction

Processes present a thermal effect during their evolution in general, and thereby the calorimetric technique allows us to determine the magnitude of these effects and the variation presented in the energetic content of the systems that develop in the mentioned processes. The physical and chemical processes that occur in a solid surface generate heat quantities that can be determined to characterize certain interactions [1–3].

Immersion calorimetry is used to determine, according to the system thermodynamic conditions, the heat that is produced when a solid and a liquid come into contact, which is tantamount to the immersion enthalpy of the contact process, which is established for a specific quantity of the solid being studied. The thermal effects resulting from immersing a solid in a solvent, generally of non-polar type with which the solid does not present chemical interactions, can be related to the surface properties of the solid considered [4–6].

The determination of the experimental immersion enthalpy can be performed in an isothermal type calorimeter that has a small thermal resistance, $R_T$, and high heat capacity of the surroundings. Thus, the flow heat is due generally to the small difference in the temperature given between the surroundings, $T_S$, and the cell, $T_C$, during the occurrence of the observed process [7], so that the heat quantity can be evaluated from temperature records, or a property proportional to this one as a function of time.

$$Q = K \int \Delta T(t)\mathrm{d}t \tag{1}$$

In many cases, it is possible to register the calibration factor $K$ as constant in the range of temperature in which the process studied is carried out [8].

Once the immersion enthalpy of the solid is known, which for this work is the activated carbon, this enthalpy is related to the volume of the micropore, $W_o$, and to the molar volume, $V_m$, of the adsorbate, by means of the Stoeckli and Kraehenbuehl equation [9]:

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

This shows that the immersion enthalpy, $\Delta H_{im}$, corresponds to the process of filling of the micropores and it is different from the wetting enthalpy of open or non-

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porous surfaces. The experimental immersion enthalpy, $\Delta H_{\text{exp}}$, of the activated carbons has two types of contribution: one due to the micropores and the other due to the external surface wetting, $S_{\text{ext}}$, as stated by Bansal et al. [10]. This can be expressed by means of the following equation:

$$\Delta H_{\text{exp}} = \Delta H_{\text{im}} + h_i S_{\text{ext}} \tag{3}$$

The experimental immersion enthalpy is a characterization parameter that will be different insofar as the physical and chemical characteristics of the solids vary; for this reason in this work the experimental immersion enthalpies of activated carbons that are obtained from lignocellulosic material, the seed of *Mucuna mutisiana*, by thermal activation with a steam-nitrogen mixture to different temperatures and activation times were determined in different calorimetric liquids. The immersion enthalpies are correlated with properties of the activated carbons such as their burn-off, surface area, micropore volume, and contents of acid and basic groups.

## Experimental

### Lignocellulosic precursor

*Mucuna* is a kind of plant of the papilionoideae subfamily and Phaseoleae group. The *M. mutisiana* seed employed in this work is mainly used for the elaboration of crafts due to its hardness and shape. It is around 3 cm in diameter, brown in color, and repulsive to insect attack [11]. For the carbonization, the seed is ground in a disc mill to a size of about 4 mm.

### Preparation of the activated carbons

The carbonization is performed by lots in a horizontal oven using a quartz cell with an approximate capacity of 150 g of lignocellulosic material. The conditions for the carbonization process are the following: carbonization temperature 450 °C, nitrogen flow 150–160 $\text{cm}^3\ \text{min}^{-1}$, heat rate 10 °C $\text{min}^{-1}$, and residence time 1 h.

The carbonized material is then subject to a gasification process with a steam-nitrogen mixture [12]. The temperature is varied between 600 and 900 °C [13] and the residence times between 1 and 10 h, with the aim of studying the effect during the activation process. The activated carbon denomination is as follows: AC: activated carbon; S: steam; the activation temperature; and finally the activation time; for example the sample ACS600-5 corresponds to an activated carbon with steam at a temperature of 600 °C for 5 h.

### Textural characterization of activated carbon

The carbonaceous samples measuring about 0.100 g are degasified at 250 °C for a period of 3 h in an Autosorb 3B, Quantachrome Co. The corresponding adsorption nitrogen isotherms are obtained with this equipment at 77 K. The surface area is determined by the B.E.T method and the micropore volume is determined by the Dubinin–Radushkevich method.

### Determination of the basic and acid sites

Total acidity and basicity of activated carbons are determined by means of the Boehm method. 500 mg of each solid is weighed, to determine both acid sites and basic sites. One sample of activated carbon is placed in a glass flask having an emery board lid with 50.0 mL of NaOH, 0.1 N, and another sample is placed in a recipient with 50.0 mL of HCl, 0.1 N. Solutions are mechanically stirred and kept at a constant room temperature of 25.0 °C for 5 days. 10.0 mL samples of each one of the solutions are taken and titrated with the standard sodium hydroxide or chlorhydric acid solutions, depending on the case; during the titration, the pH of the solution is measured with a CG 840B Schott pH meter.

### Experimental immersion enthalpy determination

In the present work, experimental immersion enthalpies of the activated carbons in different calorimetric liquids, carbon tetrachloride, water, and aqueous solutions of NaOH and HCl 2 M, are determined for the estimation of the energetic interactions when the solid is in contact with the solutions of these compounds. A heat conduction microcalorimeter equipped with a calorimetric cell made of stainless steel is used for the determination of the experimental immersion enthalpies [14]. Inside the cell, approximately 10 mL of the respective solution is set out (previously kept at 298 K in a thermostat). A 50–100-mg activated carbon sample is put in a glass bulb point inside the calorimetric cell and the microcalorimeter is assembled. When the device reaches a temperature of 298 K, it starts to record the output potential for approximately 15 min, taking data of potential every 20 s. After that, the glass bulb breakage takes place and the generated thermal effect is recorded while the potential readings continue for 15 min more. Finally, the device is calibrated electrically.

## Results and discussion

Figure 1 shows a typical thermogram obtained with a Calvet type heat conduction calorimeter as used in this work.

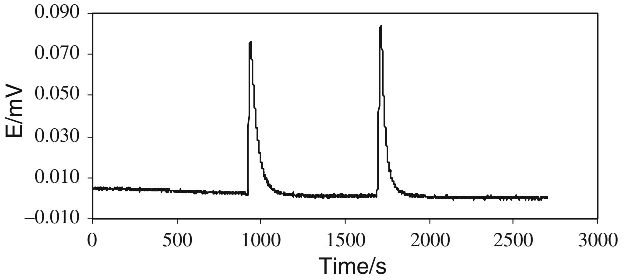

**Fig. 1** Calorimetric response obtained in the immersion of activated carbon ACS900-2 in $CCl_4$

The first peak corresponds to the heat generated by the contact of the porous solids with the respective immersion liquid and the second one corresponds to the electrical calibration when an electrical work is supplied during a measured time. For a relation between the areas under the peaks it is possible to determine the value of the solid immersion enthalpy [15].

The results obtained for the experimental immersion enthalpies in $CCl_4$, $H_2O$, NaOH, and HCl 2 M solutions are shown in Table 1; it is observed that the values for the experimental immersion enthalpy of the activated carbons in $CCl_4$ are due to the interaction of the solid surface with the liquid. In general, they are higher than when they come into contact with water in which the surface chemical groups occur. Such values agree with those reported by other authors [16].

With regard to the values of the experimental immersion enthalpy of the activated carbons in solutions of HCl and NaOH, the results show that there is a major interaction of the solids with the acid solution, and, for instance, for the series of activated carbons at 700 °C in which the activation times were slightly modified, the interaction with the two solutions is similar to or greater than that for the acid solution, which shows that the content of basic groups is similar to or greater than that of the acid groups such as is obtained in the Boehm [17] type of titration, in which for such a series the content of acid groups is between 0.401 and 0.770 mmol $g^{-1}$ and for a series of basic groups it is between 0.959 and 1.694 mmol $g^{-1}$.

The activated carbons are obtained at different temperatures and activation times with the purpose of knowing the effect of these variables on their structure and relating the changes with the immersion enthalpies in order to establish the variations in the energetic interaction: solid–liquid. The percentage of burn-off [18] is a variable that indicates the degree of activation of the carbonized material; in Fig. 2, the experimental immersion enthalpy of the activated carbons of series ACS700 in $CCl_4$ as a function of the burn-off percentage is related. It was observed that as the percentage of burn-off increases, the value of the experimental immersion enthalpy increases due to a major porosity of the activated carbons having been formed; the light, clear colored line shows the trend. These results are similar to those obtained in earlier works [19].

Other important variables that characterize the activated carbons are the surface area determined by the B.E.T. model and the micropore volume determined by the D.R. model. In turn, these are related to the experimental immersion enthalpy in solvents with which the solid surface does not present a reaction as in this case of $CCl_4$. In Figs. 3 and 4, the relations between the experimental immersion enthalpy of the activated carbons as a function of the area B.E.T and the micropore volume are shown.

**Table 1** Experimental immersion enthalpy of the activated carbons

| Sample | $-\Delta Hi_{\mathrm{exp}}$ $CCl_4$/$Jg^{-1}$ | $-\Delta Hi_{\mathrm{exp}}$ $H_2O$/$Jg^{-1}$ | $-\Delta Hi_{\mathrm{exp}}$ HCl/$Jg^{-1}$ | $-\Delta Hi_{\mathrm{exp}}$ NaOH/$Jg^{-1}$ |
|---|---|---|---|---|
| ACS600-5 | 4.02 ± 0.16 | 7.65 ± 0.31 | 13.2 ± 0.5 | – |
| ACS600-10 | 10.1 ± 0.4 | 11.8 ± 0.5 | 18.9 ± 0.8 | 9.15 ± 0.36 |
| ACS700-1 | 27.0 ± 1.1 | 12.8 ± 0.5 | 17.9 ± 0.7 | 17.3 ± 0.7 |
| ACS700-3 | 34.1 ± 1.4 | 10.6 ± 0.4 | 22.6 ± 0.9 | 22.2 ± 0.9 |
| ACS700-4 | 35.8 ± 1.4 | 15.6 ± 0.6 | 23.5 ± 0.9 | 25.9 ± 1.0 |
| ACS700-6 | 41.0 ± 1.6 | 33.3 ± 1.3 | 23.6 ± 0.9 | 20.4 ± 0.8 |
| ACS700-7 | 39.8 ± 1.6 | 23.2 ± 0.9 | 24.5 ± 1.0 | 27.0 ± 1.1 |
| ACS700-8 | 39.9 ± 1.6 | 10.9 ± 0.4 | 31.4 ± 1.3 | 21.0 ± 0.8 |
| ACS700-9 | 47.8 ± 1.9 | 20.6 ± 0.8 | 47.9 ± 1.9 | 29.2 ± 1.2 |
| ACS800-1 | 44.1 ± 1.8 | 32.4 ± 1.3 | 62.6 ± 2.5 | 29.3 ± 1.2 |
| ACS800-2 | 57.1 ± 2.3 | 41.6 ± 1.7 | 70.6 ± 2.8 | 54.5 ± 2.2 |
| ACS800-3 | 47.6 ± 1.9 | 48.8 ± 1.9 | 52.7 ± 2.1 | 42.4 ± 1.7 |
| ACS900-1 | 63.9 ± 2.6 | 48.9 ± 1.9 | 66.7 ± 2.7 | 44.2 ± 1.8 |
| ACS900-2 | 75.2 ± 3.0 | 53.5 ± 2.1 | 84.3 ± 3.4 | 48.3 ± 1.9 |

The results are the average of three determinations

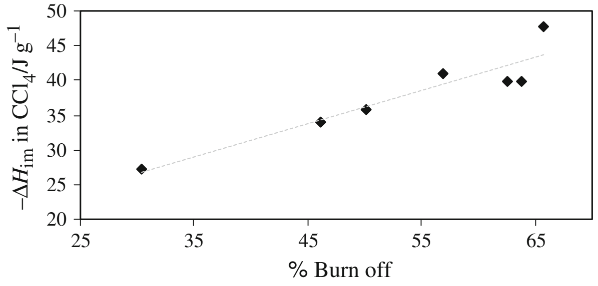

**Fig. 2** Experimental immersion enthalpy of ACS700 activated carbons as a function of burn-off

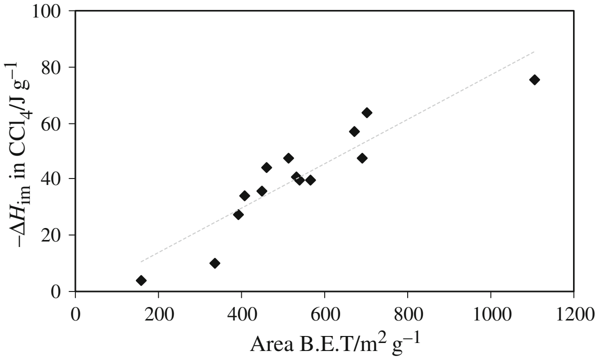

**Fig. 3** Experimental immersion enthalpy of the activated carbons in $CCl_4$ as a function of area B.E.T

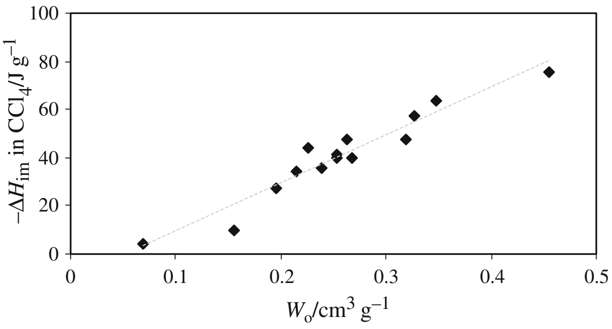

**Fig. 4** Experimental immersion enthalpy of the activated carbons in $CCl_4$ as a function of micropore volume

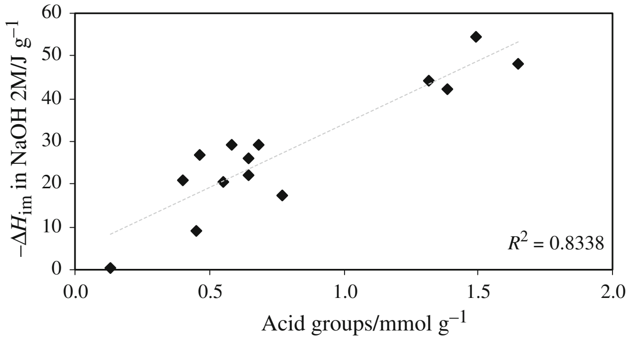

**Fig. 5** Experimental immersion enthalpy of the activated carbons in NaOH solution as a function of acid groups

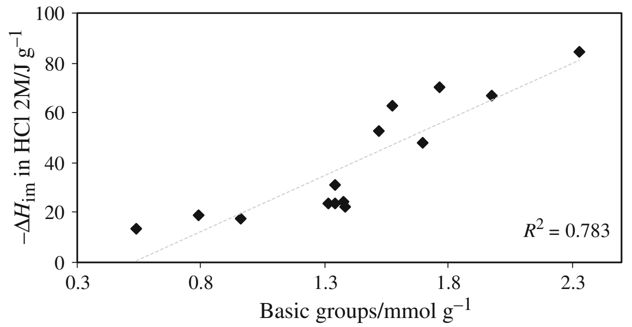

**Fig. 6** Experimental immersion enthalpy of the activated carbons in HCl solution as a function of basic groups

Also in the graphs, the lines are shown as an indication of the trends, since it is observed that in Fig. 3 the experimental points show a greater dispersion, with a correlation coefficient of 0.8401, compared with the relation between the experimental immersion enthalpy and the micropore volume, with a correlation coefficient of 0.9276, as shown in Eq. 2 in which the micropore volume, $W_o$, is proportional to the experimental immersion enthalpy solid that is totally microporous.

Another important parameter of characterization is the surface chemistry of the activated carbon that is represented in the content of acid and basic total groups, and therefore the values of the experimental immersion enthalpies in HCl and NaOH solutions correspond to the energetic interaction with the basic and acid groups, respectively. Figure 5 shows the experimental immersion enthalpy of the activated carbons in NaOH 2 M solution in relation to the content of acid groups, in which dispersion with regard to the line is observed, because the value of the experimental immersion enthalpy is the result of several effects such as the chemical groups with the solvent water, the ions along with surface effects, and water competition for the specific groups.

Finally, Fig. 6 shows the relation between the experimental immersion enthalpy of the activated carbons in HCl solution and the content of basic groups. It is observed that for some carbons the values of the experimental immersion enthalpy in HCl solution are greater than for the immersion in NaOH solution because this interaction is due not only to the oxygenated surface groups of basic character, such as pyrone or chromene, but also to the origin of the positive surface charge of the carbon produced by regions rich in electrons $\pi$ inside the graphene layers acting as Lewis basic centers, which accept protons of the aqueous solution [20], releasing energy measured by the calorimeter.

## Conclusions

The experimental immersion enthalpies of 14 activated carbons with different burn-offs are determined, with values between 4.0 and 75.2 J $g^{-1}$ for the immersion in $CCl_4$, 7.6 and 53.5 J $g^{-1}$ for the immersion in water, 13.2 and 84.3 J $g^{-1}$ for the immersion in NaOH solution 2 M, and 9.15 and 48.3 J $g^{-1}$ for the immersion in HCl solution 2 M.

An increase in the values of the experimental immersion enthalpy of the activated carbons in $CCl_4$ with the increase in the surface area B.E.T. values and with the increase in the micropore volume values was observed. This experimental immersion enthalpy also increases with the increase in the percentage burn-off of the activated carbons, since with the increase in the burn-off, the solid porosity is modified.

The experimental immersion enthalpy values in acid solution are greater than those obtained in basic solution, showing a greater interaction with surface basic sites of the activated carbons, which show this characteristic in the preparation conditions.

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