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IMMERSION ENTHALPY OF CARBONS ACTIVATED IN AQUEOUS SOLUTIONS OF AROMATIC COMPOUNDS

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ABSTRACT

Activated carbons are prepared from lignocellulosic materials by carbonization and posterior activation using CO_2 at 900 °. Under these conditions, materials with an activation percentage between 20 to 30 %, corresponding to a development of superficial area of 274 to 423 m^2g^{-1} are obtained.

It is established that activated carbons are of basic character and give pH values in the point of zero charge, pH_{PZC}, that range between 7.4 y 9.7 and total basicity contents higher in all cases than the values obtained for the total acidity; information complemented with the obtained results for the immersion enthalpies of the activated carbons in 0.1 M NaOH and HCl solutions, that present higher values for the immersion enthalpies in HCl solution.

Immersion enthalpy for the activated carbons in CCl_4 and water is determined, giving higher values for the immersion process of CCl_4, being between 31.4 and 48.6 Jg^{-1}.

Key words: Phenols adsorption, acidity and basicity, immersion calorimetry

INTRODUCTION

Calorimetry is a technique that enables the acquisition of information corresponding to the interactions produced between a solid and different immersion liquids, and the intensity of the heat effect allows the establishment of comparisons and relationships among different characteristics of the porous solids. Thus, the determination of heat immersion, under certain specific conditions, constitutes an additional parameter in solid characterization, such as the surface area, pore volume, active site content, among others (1).

In the immersion calorimetry the thermal effects resulting from the immersion of a solid into liquid, generally of a non-polar type, with which the solid does not develop chemical interactions, are measured. These immersion heats may be related to the superficial area of the considered solid, by means of the models developed by Dubinin and Stoeckli (2,3).

When other type of immersion liquid is used, information about the interactions with the chemical surface produced between the solid and the liquid is obtained; this situation arises when solutions are used with different solutes that may be acids, basis, organic compounds and metallic ions, as wetting liquid; in this case the value of the determined heat involves the interactions of the liquid and the dissolved substances with the superficial functional groups, which are of a specific type, and therefore, of a different magnitude than when a non-interacting solvent is used (4).

In this work, five samples of activated carbon obtained by physical activation, with activation rates of about 20% are studied; from which samples the point of zero charge, the total contents of acid and basic groups, the immersion heat in CCl_4 and water, the immersion enthalpy and adsorption in phenol and 4-nitro phenol aqueous solutions are determined. With the obtained results a hydrophobic factor is calculated, which indicates the influence of the activated carbon surface condition in the interaction between such carbon and the phenol and 4-nitro phenol aqueous solutions.

METHODOLOGY

The characteristics of activated carbons used in this study are show in the Table 1. I this, the precursor material, denomination, activation rate and surface area of activated carbons studied in this paper are shown.

Table 1. Characteristics of Activated Carbons

Precursor	**Denomination**	**Activation rate**	**Surface Area (m^2g^{-1})**
African palm stone	CACu	18	274
Coconut peel	CACo	21	292
Pine wood	CAM	28	423
Peach seed	CAD	24	323
Husks of sugar cane	CAB	23	385

Determination of the Basic and Acid sites

Total acidity and basicity of activated carbons are determined by means of the Boehm method (5). 1.000 g of each solid is weighed, and is placed in a glass flask with 50.0 mL of NaOH, 0.1 N or HCl, 0.1N. Solutions are mechanically stirred and kept at constant room temperature of 25.0 °C, for 5 days. 10.0mL samples of each one of the solutions are tittered with solution of sodium hydroxide or chlorhydric acid, depending on the case; with a CG 840B Schott pH meter.

Determination of Point of Zero Charge, PZC. Mass tittering method

Activated carbons quantities are weighed, within a range of 0.010 to 0.600 g, each one of them is placed in a glass flask of 50.0 mL and 20.0 mL of NaCl, 0.1 M is added. Flasks are covered and mechanically stirred at constant room temperature of 25.0 °C for 48 hours, so that the carbon charges may reach a balance. After 48 h the pH of each one of the solutions is measured with a CG 840B Schott pH meter.

Determination of the adsorbed phenol and 4-nitro phenol quantities.

In order to determine the phenol and 4-nitro phenol quantities adsorbed by each activated carbon, 0.500 of the latter is placed in glass flasks with 250 mL of the aqueous solutions of phenol and 4-nitro phenol with a concentration of 100 $mg.L^{-1}$. Samples are mechanically stirred and kept at room temperature of 25.0 °C, for 72 h. The solution balance concentration after the adsorption is determined, after calibration with a spectrophotometric equipment uv-vis Milton Roy Co. Spectronic Genesys SN.

Determination of the immersion heat

In this paper, determinations of heat immersion of activated carbons in different calorimetric liquid, such as: CCl_4, water and aqueous phenol and 4-nitro phenol solutions of 100 $mg.L^{-1}$ to determine energetic interactions when the activated carbon is in contact with the solutions of such compounds, are performed. In order to determine the immersion heats, a heat conduction microcalorimeter with a stainless calorimetric cell is used (6).

RESULTS AND DISCUSSION

In the Figure 1, a typical graphic of potential in function of time for the immersion of activated carbon obtained from pine wood, CAM in CCl_4 , is shown, in the first peak the slope corresponds to the effect produced by solid wetting with solvent and the second pike is produced by the electric calibration.

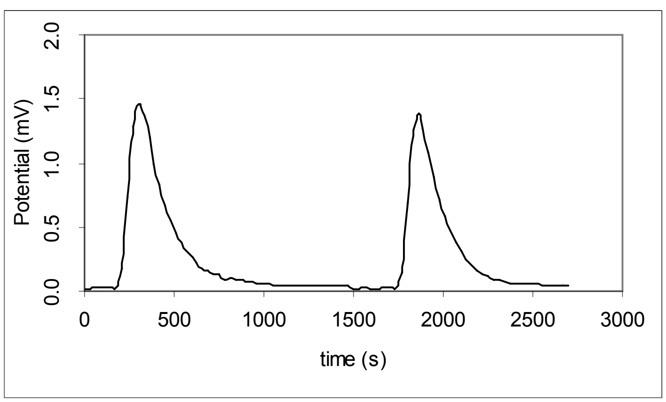

Figure 1. Thermogram obtained in the immersion of activated carbon CAM in CCl_4

From the immersion heats in CCl_4 and in water, the hydrophobic factor, hf, is calculated, that is obtained as the relationship between the immersion heat of the CCl4 immersed sample and the respective water immersion heat; therefore, hf high values indicate that the activated carbon surface shows a lower interaction with water. The results are show in Table 2.

Table 2. Surface chemical characteristics of activated carbons.

Activated carbon	**Total acid Sites ($meqg^{-1}$)**	**Total basic Sites ($meqg^{-1}$)**	**pH_{PZC}**	**-ΔHimm CCl_4 (Jg^{-1})**	**-ΔHimm H_2O (Jg^{-1})**	**Hydrophobic Factor**
CACu	0.21	0.48	8.9	31.4	9.20	3.43
CACo	0.42	0.76	7.8	33.6	8.60	3.91
CAM	0.48	0.56	7.4	48.6	7.20	6.75
CAD	0.11	0.68	9.7	37.2	12.5	2.98
CAB	0.29	0.63	9.2	44.3	10.4	4.26

In Figure 2, the relationship between the immersion heats in CCl_4 in function of the hydrophobic factor is described, it is observed that while the hydrophobic factor increases, the immersion heat in CCl_4 increases, and the water immersion heat decreases; the activated carbon showing the highest hydrophobic value, of 6.75, is CAM which in turn shows a similar acid and basic sites content.

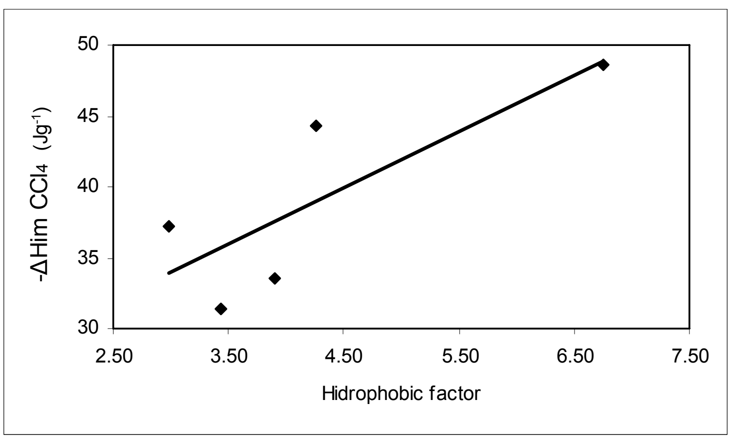

Figure 2. Immersion heats in CCl_4 in function of the hydrophobic factor.

In Table 3 the results obtained for the phenol and 4-nitro phenol adsorption in activated carbons, in mgg^{-1} and the immersion enthalpy, ΔHimm, in aqueous solutions of such compounds with a concentration of 100 $mg.L^{-1}$, en Jg^{-1} are shown.

Table 3. Adsorption and immersion enthalpy of aqueous solutions of phenol and 4-nitro phenol in activated carbons.

Activated carbon	**Adsorbed phenol quantitly (mgg^{-1})**	**Adsorbed 4-nitro phenol quantity (mgg^{-1})**	**$-\Delta Himm$ phenol (Jg^{-1})**	**$-\Delta Himm$ 4-nitro phenol (Jg^{-1})**
CACu	19	37	10.2	18.6
CACo	15	30	9.50	12.7
CAM	12	21	7.60	10.3
CAD	23	42	13.9	20.5
CAB	17	41	12.4	17.8

Figure 3 shows the relationship established between the pH in the point of zero charge, pH_{PZC}, and the hydrophobic factor, hf, it is observed that while the fh values are higher, pH_{PZC} tend to reach a neuter value, either because the content of acid and basic sites are similar or because the content of basic sites is higher and such sites are related to electron π rich zones inside the graphenic-typer layers, which act as Lewis bases (7).

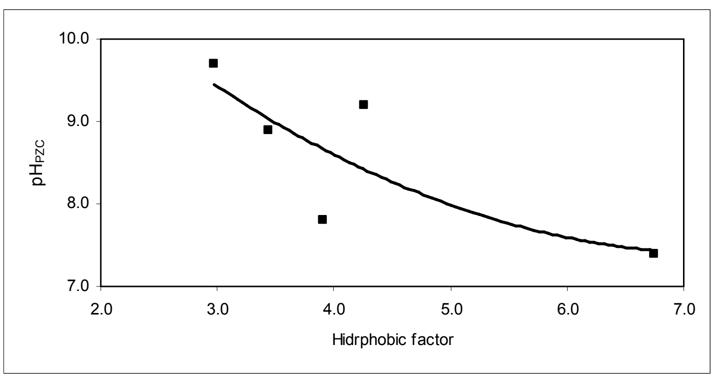

Figure 3. Relation between pH_{PZC} and hydrophobic factor

The relationship between the immersion enthalpies of the activated carbons in the solutions of the phenolic compounds and the hydrophobic factor is shown in the Figure 4. It is observed that, while the hydrophobic factor increases, the immersion heat for the solutions of both compounds decreases, this is because the interaction between carbon surface with an aqueous phase is lower because the surface chemical groups relationship is changed.

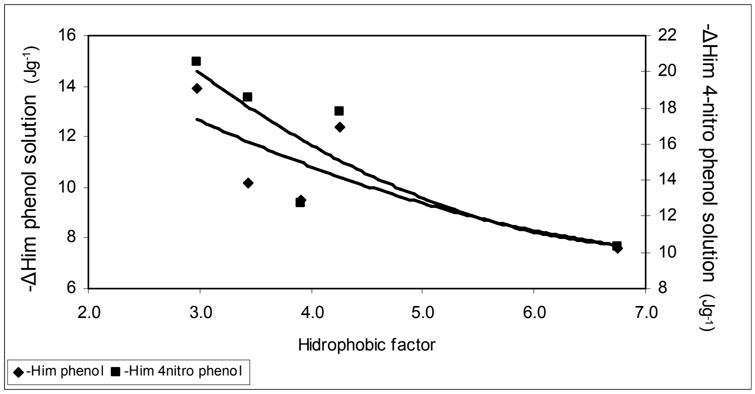

Figure 4. Relationship between the hydrophobic factor and the immersion heat of activated carbons in phenol and 4-nitro phenol aqueous solutions.

CONCLUSIONS

The interactions among five samples of activated carbon, obtained from several lignocellulosic materials and with a moderate activation level, and aqueous solutions of phenol and 4-nitro phenol are studied by means of the determination of the immersion enthalpies.

It is established that the obtained activated carbons are of a basic nature and show values for the point of zero charge, that range between 7.4 and 9.7 and contents of total basicity higher in all cases than the values obtained for the total acidity. Likewise, the immersion enthalpy of the activated carbons in CCl_4 and water is determined with higher values for immersion enthalpy in CCl_4 that range between 31.4 and 48.6 Jg-1.

From the immersion heats the hydrophobic factor is calculated, hf, that ranges between 2.98 and 6.75 for the studied activated carbons.

The immersion enthalpies in phenol range between 7.6 and 13.9 and for the case of 4-nitro phenol, between 12.7 and 20.5; with all the samples showing higher values upon immersion in the second compound.

It is observed that the heat effect produced between the activated carbons and the adsorbed phenolic compound solutions decreases with the acid groups content and that the immersion enthalpy of the activated carbons in aqueous solutions of the mentioned compounds increases when the PZC value increases. As regards the hydrophobic factor, immersion heat of the samples decreases when such parameter increases, because the interaction between the phases is lower.

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