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CALORIMETRIC DETERMINATION OF ACTIVATED CARBONS IN AQUEOUS SOLUTIONS

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The interactions among five samples of activated carbons, obtained from different lignocellulosic materials with different degrees of activation of approximately 20% and aqueous solutions of phenol and 4-nitro phenol are studied by means of the determination of immersion enthalpies.

It is established that the obtained activated carbons are of a basic character and show values for the pH at the point of zero charge, pH_{PZC}, that range from 7.4 to 9.7 and, in all cases, higher total basicity contents than the values obtained for total acidity.

The immersion heat of the activated carbons in CCl_4 and water is determined obtaining values which are higher for CCl_4 immersion and vary from 31.4 to 48.6 J g^{-1}. The hydrophobic factor, *hf*, it is calculated from the relation between of the immersion heat of the activated carbons in CCl_4 and the immersion heat in water, the obtained values were 2.98 and 6.75, which are greater than 1 due to the greater values obtained in CCl_4 when compared to the values obtained in water.

Immersion enthalpies in phenol solution range from 7.6 to 13.9 J g^{-1} and for the case of 4-nitro phenol such enthalpies range from 12.7 to 20.5 J g^{-1}; all the 5 samples studied showed a higher value for the heat of immersion in aqueous solutions of 4-nitro phenol.

Keywords: *acidity, basicity, immersion calorimetry, immersion enthalpy, phenol adsorption, pzc*

Introduction

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 [1, 2].

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 [3].

The determination of the immersion heats of activated carbons in liquids that possess different molecular sizes has enabled a characterization according to pore size distribution, as a complementary method to the gas adsorption one which is the most frequently used [4].

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 [5, 6]. 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 [7, 8].

One of the applications of the activated carbons is the removal of water organic compounds, and for this particular application one of the most influential aspects in adsorption is surface chemistry [9], which depends on the heteroatom content, mainly on the presence of oxygen groups, which determine the surface charge in the activated carbons, hydrophobicity and electronic density of the graphite-type layers. Surface charge depends on the medium pH and on the carbon surface characteristics; negative surface charge is caused by the dissociation of the surface groups of an acid nature, such as the phenolic and carboxylic groups. The positive charge is not attributed to very specific surface groups and may be constituted by groups of a basic nature such as pyrones or chromens or by the presence of surface zones having a strong presence of π electrons which act as Lewis bases [10].

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In this paper, five samples of activated carbon obtained by physical activation, with activation percentages 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.

Experimental

The activated carbons used in this study were obtained by physical activation of different lignocellulosic materials, under the same experimental conditions so that the final surface characteristics of each one of them are caused by the nature of the precursor material [11]. In Table 1: the precursor material, denomination, activation rate and surface area of activated carbons studied in this paper are shown.

Determination of the basic and acid sites

Total acidity and basicity of activated carbons are determined by means of the Boehm method [12]. 1.000 g of each solid is weighed, both to determine acid sites and basic sites. One sample of activated carbon is placed in a glass flask having an emery boarded 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 constant room temperature of 25.0°C, for 5 days. 10.0 mL samples of each one of the solutions are taken and tittered with the standard solution of sodium hydroxide or chlorhydric acid, depending on the case; during the tittering the pH of the solution is measured with a CG 840B Schott pH meter.

Determination of pH at the 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 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 h, 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 [13].

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. Below, a general description of the manner in which such determinations are made is provided.

In order to determine the immersion heats, a heat conduction microcalorimeter with a stainless calorimetric cell is used, which has a calorimeter constant K of 51.08±0.92 W V^{-1} [14]. In the cell, 30 mL of the solution being used is placed, which has been kept in a thermostat at 25.0°C; a sample of activated carbon is weighed and placed in a calorimetric cell in a glass ampoule, and the microcalorimeter is assembled. When the equipment reaches a temperature of about 25°C, the outcoming potential record is started for a period of approximately 15 min with potential readings every 20 s; afterwards the glass ampoule is broken, the generated thermal effect is recorded and the readings corresponding to the potential are continued for approximately 15 more minutes, finally electrical calibration is performed.

Table 1 Characteristics of activated carbons

Precursor	Denomination	Activation rate	Surface area/m^2 g^{-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

Results and discussion

The activated carbons are prepared by carbonization under nitrogen atmosphere and further activation with CO_2 at 900°C for a period of 2 h, under these conditions; materials with a high activation rate of about 20–30% are obtained. This value corresponds to a moderate surface development [15].

The analysis is then focused on the surface chemistry of the activated carbons that depends largely on the heteroatom contents, which in turn determine the surface charge, its hydrophobicity, total acidity and total basicity, and such factors intervene in the adsorption capacity of activated carbon [16]; therefore, the content of surface groups has been determined, the pH in the point of zero charge, pH_{PZC}, and the immersion heat of the activated carbons in CCl_4 and in water in order to relate them to the phenol and 4-nitro phenol activity adsorption in aqueous solution. In Fig. 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.

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 CCl_4 immersed sample and the respective water immersion heat; therefore, *hf* high values indicate that the activated carbon surface shows a lower interaction with water. In Table 2, the results obtained are shown, for total acidity and basicity, in meq g^{-1}, the pH in the point of zero charge, pH_{PZC}, the immersion enthalpies in CCl_4 and in water, in J g^{-1} and the hydrophobic factor *hf*.

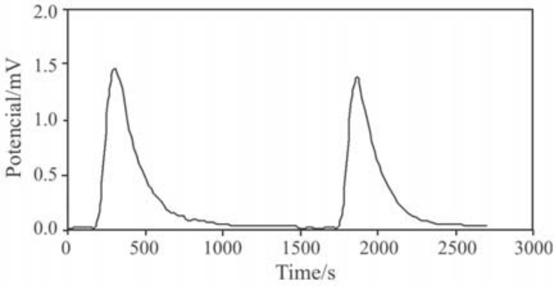

Fig. 1 Slope obtained in the immersion of activated carbon CAM in CCl_4

As it is observed in Table 2, the five samples of activated carbons show acidity contents in an approximate range between 0.10 and 0.50 meq g^{-1}; total basicity ranges from 0.48 to 0.76 meq g^{-1} which shows the basic nature of thermally obtained activated carbons under the described conditions, nevertheless differences between acidity and basicity are not great, and it is a behavior comparable to the results obtained in previous works and also by other authors [17, 18].

Regarding the pH value in the point of zero charge, pH_{PZC}, this is basic for all the activated carbons and allows its classification as type H activated carbons, thus if solids are placed in contact with solutions having a pH lower than pH_{PZC}, surface charge will be positive on the average, as in the case of this study, since the determinations of adsorption quantity and immersion calorimetry are carried out without pH adjustment.

Values for immersion heat are higher in all the cases when the liquid is CCl_4, owing to the type of existing water-surface interactions, Rutherford [19] shows a model in which water molecules occupy active sites and promote adsorption on such sites and neighboring areas.

In Fig. 2, the relationship between the immersion heats in CCl_4 (Fig. 2a) and in water (Fig. 2b) 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. The graphics show trend lines with *R* (correlation coefficient) values of approximately 0.6, for the 5 different samples of activated carbon, indicating the influence of the type of interaction between the solid and the immersion liquid.

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 *hf* values are higher, pH_{PZC} tend to reach a neuter

Table 2 Surface chemical characteristics of activated carbons

Activated carbon	Total acid sites/ meq g^{-1}	Total basic sites/ meq g^{-1}	pH_{PZC}	$^{a}-\Delta H_{imm}$ CCl_4/ J g^{-1}	$^{a}-\Delta H_{imm}$ H_2O/ J g^{-1}	Hydrophobic factor
CACu	0.21	0.48	8.9	31.4±1.92	9.20±0.56	3.43
CACo	0.42	0.76	7.8	33.6±1.88	8.60±0.62	3.91
CAM	0.48	0.56	7.4	48.6±2.33	7.20±0.54	6.75
CAD	0.11	0.68	9.7	37.2±1.96	12.5±0.74	2.98
CAB	0.29	0.63	9.2	44.3±2.12	10.4±0.64	4.26

[a]corresponds to the average of 5 measurements and their respective standard deviations

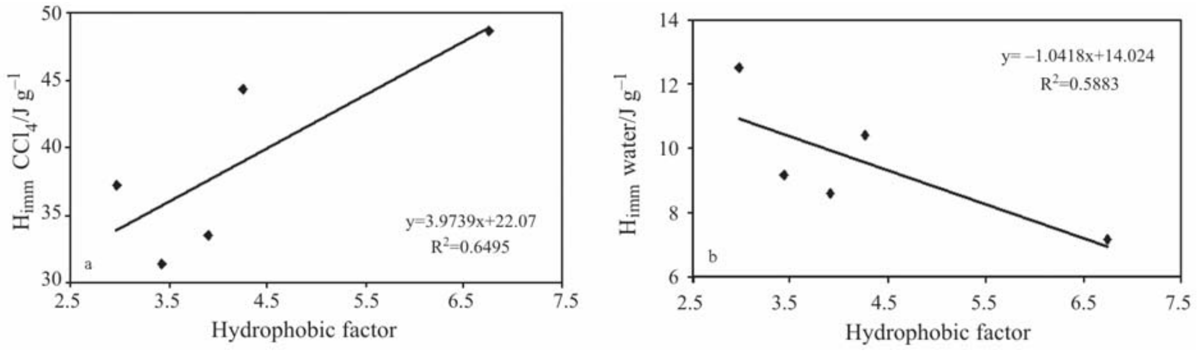

Fig. 2 Immersion heats in CCl_4 and in water in function of the hydrophobic factor

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 [10].

The tendency line drawn to average the behavior of the experimental points correspond to a second degree polynomial, with a correlation quotient of 0.614 because of the dispersion of the CACo and CAB samples, with respect to the tendency line.

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

It is observed that adsorption is higher in all the cases for the 4-nitro phenol than for the phenol and therefore, immersion heats, of exothermical nature, are also higher when activated carbon immersion is performed in the solution of 100 mg L^{-1} of 4-nitro phenol, because the determinations have been carried out under similar experimental conditions a higher interaction is present between the activated carbons and the 4-nitro phenol solution. Similar results have been previously reported for the immersion heat of carbonaceous materials in aqueous solutions of metallic ions [20].

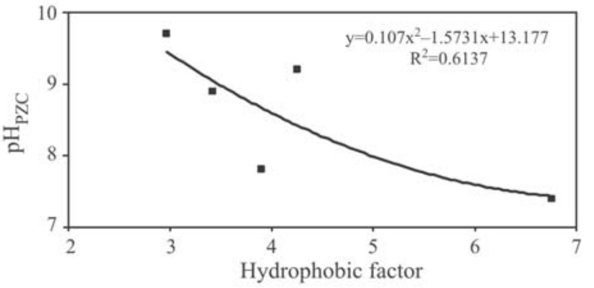

Fig. 3 Relation between pH_{PZC} and hydrophobic factor

In Fig. 4, the immersion heat of the activated carbons in the phenol solution (Fig. 4a) and the pH value in the point of zero charge, pH_{PZC}, (Fig. 4b) in function of the quantity of adsorbed phenol is shown, it is observed that while the quantity of adsorbed phenol increases, both the immersion enthalpy as the pH_{PZC} increase in a similar linear tendency which indicates that adsorption, under working experimental conditions, is favoured when activated carbons have pH_{PZC} higher values, that is to say, when surface characteristics are basic. In the case of 4-nitro phenol, immersion enthalpy and pH_{PZC} value show a similar behaviour, with a linear correlation quotient between immersion enthalpy and the adsorption quantity of the higher compound also indicating that adsorption is higher in the activated carbons of a basic nature.

Figure 5 shows the relationship between the immersion enthalpy of the activated carbons in aqueous solutions of phenol (Fig. 5a) and 4-nitro phenol (Fig. 5b) in function of the content of the surface acid groups, such graphics show that, with the increase of the acid group content the interaction of the activated carbon with the phenol solution decreases; in this point, it should be taken into account that the five activated carbons are positively charged, and an electrostatic attraction will not be caused by the phenolic compound [10].

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

Activated carbon	Adsorbed phenol/ mg g^{-1}	Adsorbed 4-nitro phenol/ mg g^{-1}	$^{a}-\Delta H_{imm}$ phenol/ J g^{-1}	$^{a}-\Delta H_{imm}$ 4-nitro phenol/ J g^{-1}
CACu	19	37	10.2±0.62	18.6±0.56
CACo	15	30	9.50±0.64	12.7±0.79
CAM	12	21	7.60±0.58	10.3±0.58
CAD	23	42	13.9±0.86	20.5±0.52
CAB	17	41	12.4±0.78	17.8±0.55

^{a}corresponds to the average of 5 measurements and their respective standard deviations

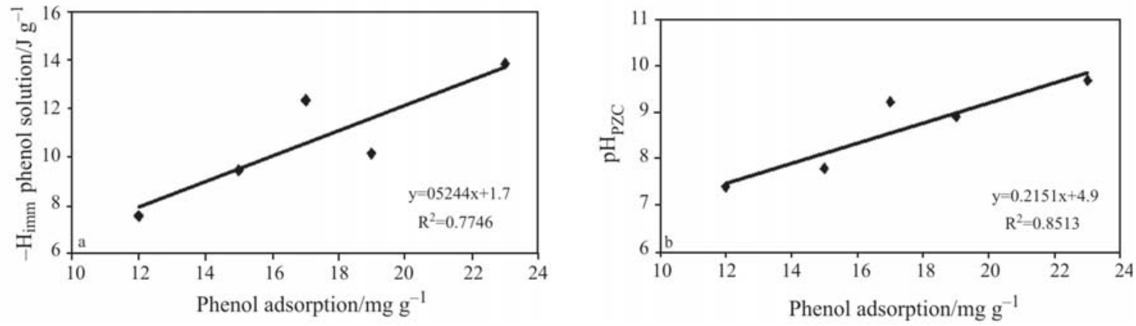

Fig. 4 Immersion enthalpy of activated carbons in aqueous solution of phenol and pH_{PZC} in function of the phenol adsorbed quantity

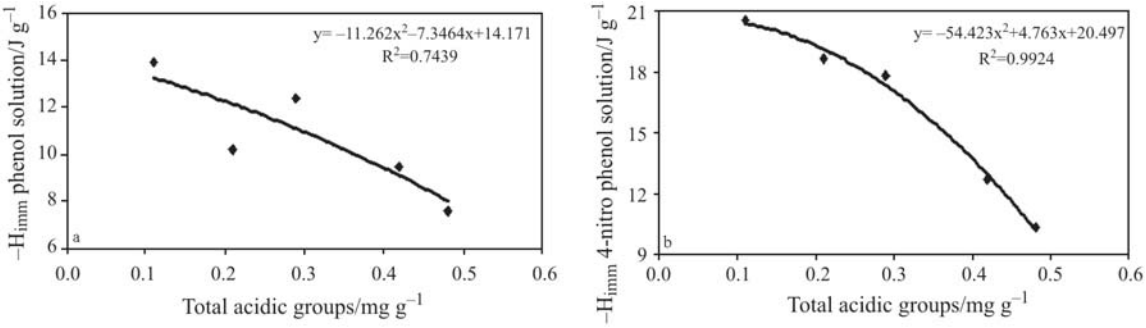

Fig. 5 Immersion enthalpy of activated carbons in aqueous phenol solutions in function of the total acid groups

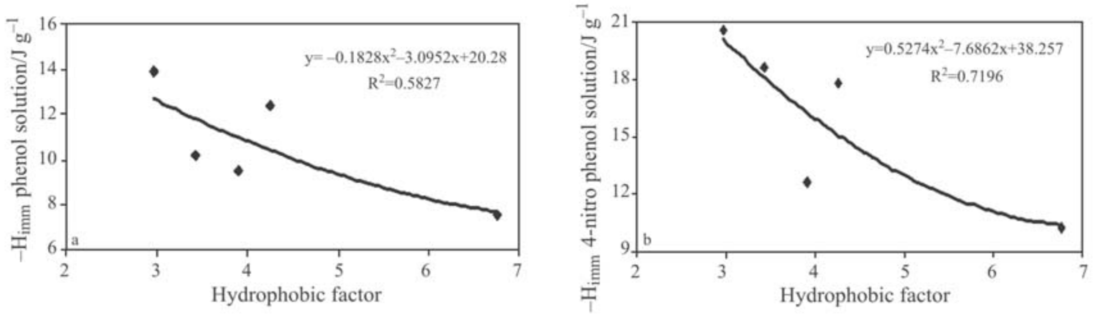

Fig. 6 Relationship between the hydrophobic factor and the immersion heat of activated carbons in phenol and 4-nitro phenol aqueous solutions

The correlation coefficient value is larger, with a value of 0.992, when the interaction occurs between the activated carbons and the 4-nitro phenol solutions.

Finally, the relationship between the immersion enthalpies of the activated carbons in the solutions of the phenolic compounds and the hydrophobic factor is shown in Fig. 6a from phenol solution and Fig. 6b from 4-nitro phenol solution. 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.

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 pH in 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 J g^{-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 J g^{-1} and for the case of 4-nitro phenol, between 12.7 and 20.5 J g^{-1}; 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 pH_{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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