MICROCALORIMETRY: APLICATION TO STUDY OF THE IMMERSION HEATS OF ACTIVATED CARBON INTO PHENOL AQUEOUS SOLUTIONS

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ABSTRACT

A heat conduction microcalorimeter is used for the determination of activated carbon immersion enthalpies in phenol aqueous solutions. The microcalorimeter is electrically calibrated with values for the calibration constant between 13.15 ± 0,43 WV^{-1} and 15.24 ± 0,28 WV^{-1} and is chemically calibrated with the HCl-NaOH neutralization reaction system, obtaining a value for the neutralization enthalpy of -56.64± 0,01 kJ mol^{-1} which agrees with literature reports.

The adsorption capacity and the immersion enthalpies of a commercial coal, Carbochem PS-30, are determined in phenol aqueous solutions of different concentration, from 10 to 100 mgL-1, at three temperatures 298, 308 y 318 K, obtaining values for the immersion enthalpies ranging between 15,00 and 36,00 Jg^{-1}, in the experimental conditions established.

INTRODUCTIÓN

On the free surface of a solid, thanks to the existence of a field of force, an increase in the concentration of the adsorbate molecules is produced, and when adsorption occurs, these are immobilized if the adsorption is localized. This process is spontaneous, so Gibbs free energy, ΔG, diminishes and, since the molecules turn to an adsorbed state, the entropy of the adsorbate-adsorbent system also diminishes. When combining these two facts and using the enthalpy variation expression, ΔH, we get:

$$\Delta H = \Delta G + T\Delta S < 0 \qquad (1)$$

which shows that the adsorption process is exothermic because

$\Delta H < 0$ [1].

Physical adsorption is that where no reaction between the adsorbate and the solid surface is produced during its course, but causes their linking by dispersion forces, polarization and dipolar and quadrupolar interactions, all balanced by dispersion forces. Physical adsorption does not perceptibly affect the structure of the solid force, so the solid can be considered a substratum which contributes to the field of forces and a surface where the molecules are placed, forming an adsorbed phase with independent characteristics for the adsorbate and the adsorbent. This physically adsorbed phase can be composed of one single layer of adsorbed molecules on the surface (monolayer adsorption), or an incipient condensation can occur, forming several layers of adsorbed molecules on the surface (multilayer adsorption) [2,3].

The adsorption of solutions on the surface of solid adsorbents is different from the adsorption of individual substances, such as gases, vapors and pure liquids, in that in the solution there are at least two components which form a compact layer on the surface. As a result, the components of the solution in this layer, when concentration changes, displace each other, thus changing the adsorption conditions [4].

Immersion calorimetry of porous solids

Immersion calorimetry is a method which permits the determination of the interactions which are produced between solids and liquids. For a microporous solid, without external surface, its immersion enthalpy in a liquid is given by [5]:

$$-\Delta H_i(T) = \int_0^1 q^{net}(T;\theta)d\theta \qquad (2)$$

where: q^{net} is the net adsorption heat, which by definition is the isosteric heat, q^{isot}, minus the vaporization enthalpy, $\Delta H_{vap,}$ of the adsorbent; θ is the fraction of the microporous cover.

Isosteric heat is the heat developed in the adsorption process when the alter is considered at constant coverage.

When a solid is submerged in a liquid which does not react with the surface, a heat quantity is generated. Said immersion heat is related to the formation of layer adsorbed with molecules of the liquid on the solid surface. The immersion heats of a solid produced in different liquids are usually different. Thus, these are related not only with the surface area available for the liquid but to the specific interaction between the solid surface and the immersion liquid [6].

Immersion enthalpy, ΔHim, is defined as the change in the enthalpy, at constant pressure, which takes place when a liquid is immersed in a liquid in which the solid does not dissolve or react [7]. Immersion enthalpy of a given solid can be measured from different starting points, which can be specified. The case might be that the surface is free and thus, an interface solid-liquid is formed during the measurement. In other conditions, the surface

can be totally or partially covered by a liquid film before the measurement, and the values of the immersion enthalpy for the system will be different [8].

Phenol adsorption on activated carbons

Activated carbons are widely used as adsorbents in decontamination processes because of their large surface area, their microporous structure, their high adsorption capacity and their chemical surface. Very frequently, water is contaminated with phenol and its derivatives and activated carbon is used as adsorbent to remove them [9].

The adsorption capacity of an activated carbon is highly influenced by the chemical nature of the surface and, it is because of the functional groups existing on the surface that activated carbon exhibits acid-base properties. The presence of surface chemical groups is due to the solid preparation methods and their subsequent treatment. Phenol adsorption on activated carbon is, therefore, determined by its chemical surface, by the solution pH, by the temperature. [10].

EXPERIMENTATION

Determination of immersion heat

To determine immersion heats, a heat conduction microcalorimeter with a stainless steel calorimetric cell [11] is used. Figure 1 shows a photography of the microcalorimeter used.

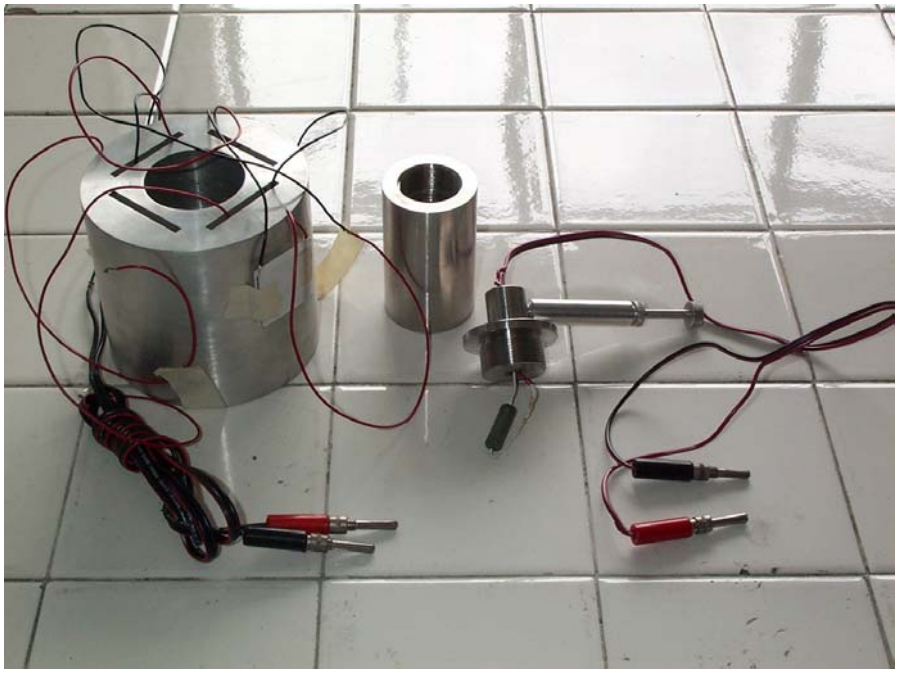

Figure 1. Heat conduction microcalorimeter with metallic cell

30 mL of the phenol solution, which has been maintained in a thermostat at work temperature, 298-308-318 K are place in the cell; a sample of carbon activated of about 0.500 g is weighed and placed inside the calorimetric cell in a glass vial; the calorimeter is assembled. When the equipment reaches the temperature established, the recording of the output potential is started for a period of approximately 15 minutes, taking potential readings every 20 seconds. The glass vial is broken, the thermal effect generated is recorded and the potential readings continue for approximately 15 more minutes. Finally it is calibrated electrically.

Determination the adsorption isotherm

To determine the adsorption curve, 0,5 g of activated carbon, Carbochem PS-30, and 250 mL of the corresponding aqueous phenol solutions (10, 20, 40, 60, 80 y 100 $mg.L^{-1}$) are placed in glass bottles, without adjusting the solutions pH. The samples are mechanically stirred and are kept at the precision measurement temperature of $\pm$ 0.1 K, for a period of approximately 15 hours. The phenol residual concentration in the solutions after adsorption is determined with a spectrophotometric equipment uv-vis Milton Roy Co. Spectronic Genesys SN.

RESULTS AND DISCUSSION

Table 1 shows the main characteristics of Carbochem™-PS30 activated carbon, which are provided by the manufacturer and which indicate its adsorption capacity.

Table 1. General characteristics of Carbochem™-PS30 activated carbon

CHARACTERÍSTIC	INFORMATIÓN
Precursor	Coconut bark
Presentation	Granular
Surface area	1080 m^2g^{-1}
Apparent density	0,5 g mL^{-1}
Ash content	5 %
Iodine number	1120

Figure 2 presents two typical thermograms which show the thermal effect generated at two different temperatures. The thin line corresponds to the thermogram of activated carbon immersion in a phenol solution of 60 mgL^{-1} when the system temperature is kept at 298 K; the thick line presents the activated carbon immersion in a solution of the same concentration as the one above, at a temperature of 318 K.

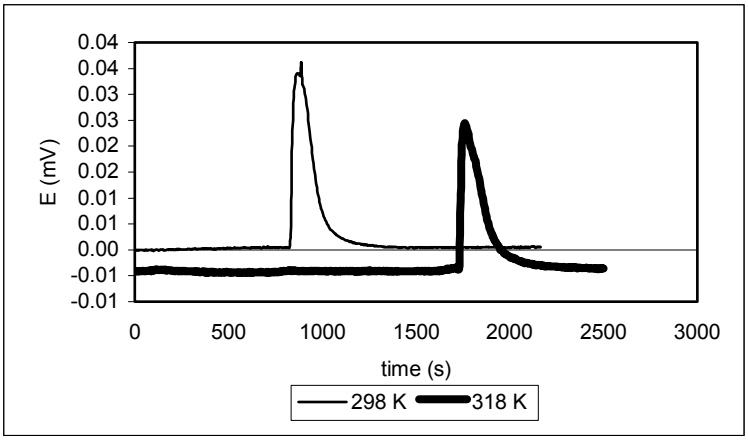

Figure 2. Thermograms obtained with the immersion of activated carbon in aqueous phenol solution at 298 and 318 K

It can be seen that the thermograms show well-defined peaks for the immersion processes and also that the effects produced are different, for the interaction between the solid and the solution is affected by the system temperature

Table 2 shows the results obtained for activated carbon immersion enthalpy at three different temperatures. The Table shows the concentration of phenol solution at which the immersion is made, Ci, in mgL^{-1}, the immersion enthalpy, ΔHim, n Jg^{-1}, and the temperature at which the determination is made.

Table 2. Activated carbon immersion enthalpies in phenol aqueous solutions at different temperatures

Phenol solution concentration Ci (mgL^{-1})	**ΔHim (Jg^{-1})**		
	298 K	**308 K**	**318 K**
10	15.25	13.45	13.74
20	16.80	15.49	13.27
40	23.68	22.15	19.87
60	31.90	30.32	27.88
80	34.36	32.63	30.19
100	35.71	33.88	31.32

The values found for the immersion enthalpies show that as the temperature is increased, the enthalpy value decreases, which indicates that the interaction solid-solution becomes smaller each time

Figure 3 presents the results obtained from the immersion enthalpy in relation to the solution concentration for each of the working temperatures.

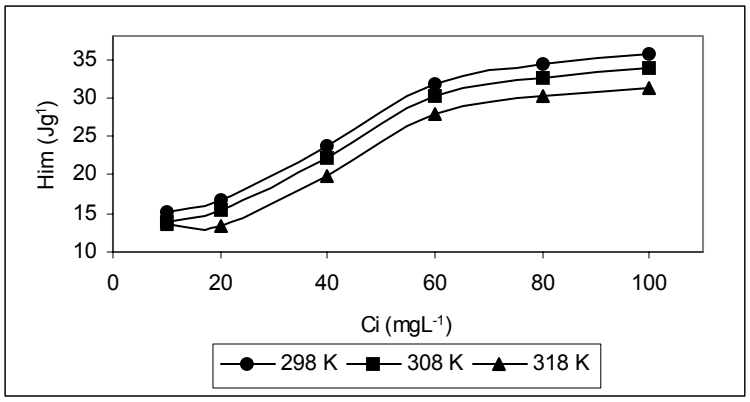

Figure 3. Activated carbon immersion enthalpies in phenol aqueous solutions at different temperatures

In Figure 3 it is observed that, even though immersion enthalpy increases when the solution concentration increases for the three temperatures studied, that does not happen regularly but it changes a little at the beginning, i.e. the heat released when the temperature is free is not the largest because there is less phenol to be adsorbed in the surface. In the central zone, the change with respect to heat is larger and it is the region where the largest phenol adsorption is produced and, at the end, the value of ΔHim is maintained, which is a result expected since the surface has become saturated with the adsorbate.

The maximum adsorption for activated carbon in phenol solutions at the same temperatures is also determined in order to observe the change that is produced in the adsorption capacity as a result of the temperature. With the results obtained Figure 4 is made, which shows the amount of adsorbed phenol in relation to the concentration of the phenol solution

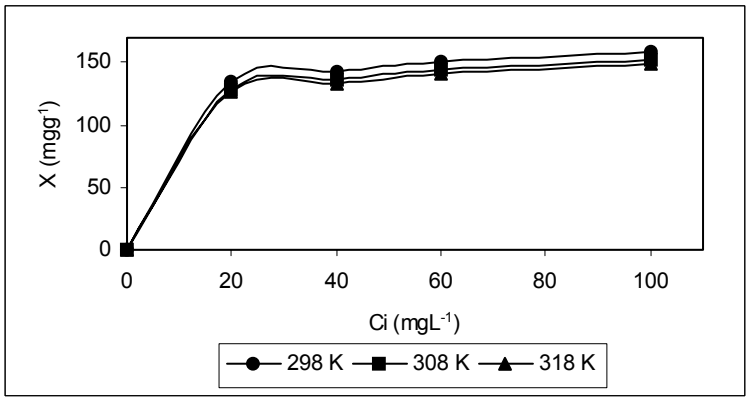

Figure 4. Activated carbon adsorption capacity in phenol aqueous solutions at different temperatures

When observing Figures 3 and 4 it can be seen that the values for immersion enthalpy change in a largest proportion than the values for phenol adsorption en each of the

temperatures, which indicates that the entalpic content of the system is more sensitive to changes of temperature and, as expected, interactions diminish with increase in temperature.

Figure 5 presents the relation between the values obtained immersion enthalpy and temperature for the different phenol concentrations used.

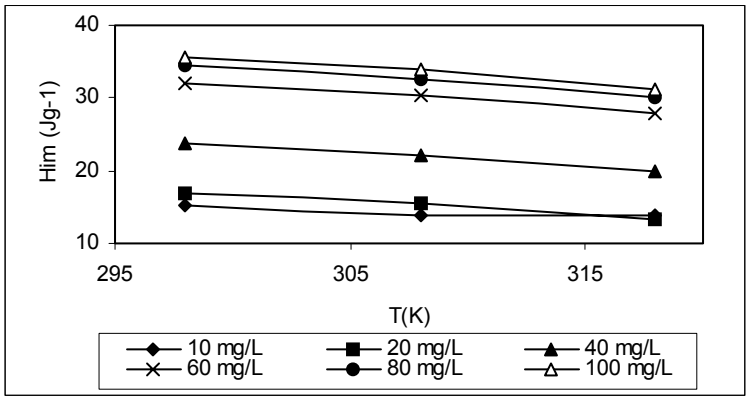

Figure 5. Immersion enthalpies according to temperature when the phenol concentration is kept constant

Figure 5 presents, for each of the concentrations of phenol solutions, straight lines with negative slopes which increase in value as the solution concentration increases. The representation shows that the initial lines are closed, in the intermediate part the lines split to finally get closed again in the high concentrations. The arrangement of these constant concentration lines indicates that there is a different interaction in the intermediate concentration zone of the range under study.

CONCLUSIONS

Immersion enthalpies are determined for activated carbon Carbochem PS-30 in phenol aqueous solutions in a concentration range between 10 and 100 mgL^{-1} and at three different temperatures of 298, 308 y 318 K, obtaining values for immersion enthalpy between 15 and 36 Jg^{-1}.

Phenol adsorption capacity on the above-mentioned activated carbon at three working temperatures is determined and adsorption values are obtained that vary between 135 and 158 mgg^{-1}.

Enthalpies and adsorption capacities are affected by temperature, with value reduction as the temperature increases.

In the concentration range studied, the greatest changes in immersion enthalpy are observed in the intermediate concentration zone.

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