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Immersion enthalpy of carbonaceous samples in aqueous solutions of monohydroxilated phenols

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Abstract The immersion enthalpies of modified activated carbons were determined, with commercial Carbochem^{TM}–PS230 (CAG) as the initial activated carbon, which was modified by: chemical treatment with HNO_3 7 mol L^{-1} (CAO) and thermal treatment under flow of H_2 (CAR) in function of the adsorbed quantity of monohydroxilated phenols, catechol, resorcinol and hydroquinone at a pH of 7 in aqueous dissolutions in order to characterize the solid–solution interaction and evaluate the influence of the chemical characteristics of the activated carbon in the phenol adsorption. The results show a variation in the immersion enthalpy in function of the adsorbed quantity of phenol and the initial dissolution concentration; which shows that the intensity of the interaction changes in function of the composition of the liquid phase. The immersion enthalpies present the following arrangement: catechol > resorcinol > hydroquinone, with a $-\Delta H_{inm}$ of 35.7; 30.8 and 24.6 Jg^{-1}, respectively, at a pH of 7 for a 100 mg L^{-1} phenol monohydroxilated solution.

Keywords Activated carbon · Hydroquinone · Immersion calorimetry · Immersion enthalpy · Oxidation · Reduction · Catechol · Resorcinol

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Introduction

The adsorption in liquid phase is a complex phenomena that requires, for best understanding, of experimental methods capable of characterizing the solid surface in terms of the superficial area, porosity, nature and energy of the adsorption sites; the technique most used for the study of the system, phenol in aqueous solution-activated carbon, is the construction of an adsorption isotherm complemented with other techniques like the TPD and immersion calorimetry, among others, giving out a more general view of the heterogeneity of the surface and the system in general [1–5].

In the immersion calorimetry the thermal effects that result from the submersion of a solid in a solvent which is generally a non-polar type, where the solid doesn't present chemical interactions, that in the case of a polar one, gives out information about the interactions with chemical groups produced by the solid and the liquid used to wet. This technique has been used over many years to precisely evaluate the energetic interactions of some solids [6–12].

The determination of immersion enthalpies of the activated carbon in different solutions, provide a direct measure if the energy involved in the process, which is not only related with the superficial area exposed to the liquid, but also to the specific interaction between the solid surface and the immersion liquid, from which the value of the enthalpy is known as a thermodynamic property used to characterize the solid–liquid interaction [11–16].

Experimental

Activated granular carbon Carbochem^{TM}–PS230, is used with the precursor being coconut shell (sample CAG).

Modifying the granular activated carbon

Thermal treatment—hydrogen (sample CAR). About 20 g of the granular activated carbon is set in the reducing system with hydrogen. This is heated to 393 K, and the pressure is reduced to 10^{-4} mmHg approximately. Later on the hydrogen is introduced. Under these conditions the oven is heated progressively until 573 for 6 days. Finally it is stored in nitrogen atmosphere.

Nitric acid treatment (sample CAO). Initially 6 g of granular activated carbon is set with a nitric acid solution 7 mol L^{-1} in a soxlet assembly at the boiling temperature of the solution; using a ratio of 60 mL of acid for every gram of carbon for a period of 9 h, afterwards the sample is washed with distilled water until a constant value of pH is reached. It is then dried at 383 K for 24 h and finally stored in a closed container in a nitrogen atmosphere.

Textural characterization and chemistry of the original activated carbon and the modified activated carbons

The carbonaceous sample of about 0.100 g, are degasified at 523 K for a 3 h period in an Autosorb 3B, Quantachrome Co equipment, where the corresponding nitrogen adsorption isotherms at 77 K were taken. Additionally the acid and basic sites were determined with the acid-basic titration of Boehm method [17] and also the zero point of charge by the mass titration method [18].

Immersion calorimetry

The study of the immersion enthalpy variation of the activated carbons is made in function of the concentration of the phenol monohydroxilated aqueous solution. The compounds of interest, catechol, resorcinol and hydroquinone, are monohydroxilated phenols, which present differences in solubility and acidity in water are influenced by the aromatic ring, as shown in Table 1, that make the interactions with the surface of the carbon be different, therefore, by the determination of the immersion enthalpies the energetic interactions in the surface of the solid in adsorption processes are quantified [12, 14–16].

Table 1 Important properties of monohydroxilated phenols [19]

Compound	pKa	Solubility (g/100 g of H_2O) a 25 °C
Catechol	9.3–13	45
Resorcinol	9.4–12.3	123
Hydroquinone	10.0–12.0	8

Determination of the immersion enthalpy

The immersion enthalpies are determined in a calorimeter isoperibolic with a cell calorimetric Dewar type and a thermistor thermometer.

Phenolic solutions: Initially 50.0 mL of aqueous solutions with the phenolic compounds at a pH of 7; in a range of 20–1,500 mg g^{-1} in a calorimetric cell and a glass cell 0.500–0.250 g of carbonaceous sample is weighed, putting together the cell and letting it reach equilibrium for approximately 40 minutes. When the variation of the leaving electric resistance of the thermistor is stable, the measures of the resistance are taken every 20 s for a period of 15 min. Then the carbonaceous samples are placed in contact with the phenolic compound solutions continuing with the measures with a final electric calibration.

Water: The measure of immersion enthalpy of the carbonaceous sample in distilled water at a pH of 7 is taken in the same procedure mentioned before.

Results and discussion

Some characteristics of the activated carbon used are shown on Tables 2 and 3. The results show how the treatments done, reduction and oxidation, do not show an appreciable variation in the textural characteristics of the carbonaceous materials, but on the other hand show changes in the electrochemical properties of the surface.

The immersion enthalpy for CAG in water at a pH of 7 was 16.6 ± 0.8 Jg^{-1}, value that makes part in the total enthalpy, since it is necessary to consider the influence of the species present in the solution of the struggle for the adsorption sites not only depend on the pH, but also on pK_a, the adsorbate molecule and the pH_{pzc} of the activates carbon, so the evaluation of the total effect turns out to be interesting [15, 16].

Figure 1 the obtained results of the immersion enthalpy, $-\Delta H_{inm}$, at a pH of 7, in functions of the amount of monohydroxilated phenols adsorbed. The differences in the values of immersion enthalpies are observed in small magnitudes; on pH 7 protonated species of monohydroxilated phenols prevail and principally dispersive interactions intervene, where the position of the hydroxyl group affect the interactions between phenols and activates carbons sample CAG, it is this way that a general tendency observed for the immersion enthalpies is the following: catechol > resorcinol > hydroquinone.

Figure 1 it is observed that the immersion enthalpy increases with the adsorbed quantity, nevertheless, a zone of greater interactions with low quantities adsorbed is present, since the immersion enthalpy turns asintotic when the retained amount is greater, given that the surface

Table 2 Textural characteristics of the activated carbons

Sample	BET surface area ($m^2\ g^{-1}$)	Vol micropore ($cm^3\ g^{-1}$)	Vol mesopore ($cm^3\ g^{-1}$)
CAG	1140	0.51	0.12
CAR	1170	0.56	0.12
CAO	1180	0.56	0.09

Table 3 Superficial chemistry of the activated carbons

Sample	pH_{PZC}	Total acidity ($mmol\ g^{-1}$)	Total basicity ($mmol\ g^{-1}$)
CAG	9.8	0.30	0.60
CAR	10.1	0.20	0.61
CAO	4.3	1.26	0.25

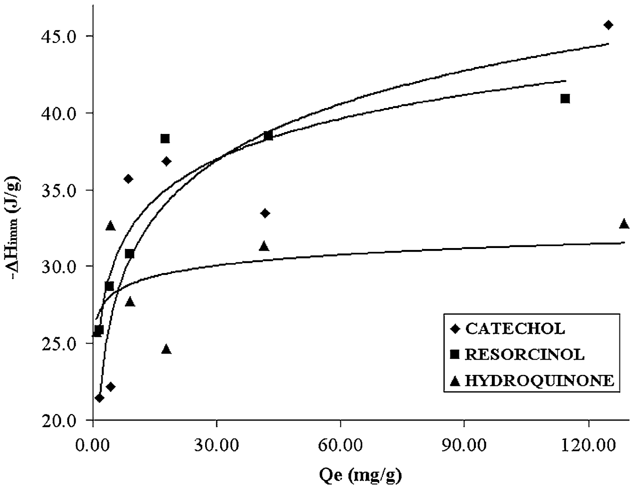

Fig. 1 Immersion enthalpies of CAG in function of phenols adsorbed quantity at pH 7

saturates with the adsorbate, so for example, for the catechol the immersion enthalpy increases with the retained amount like 21.5–45.7 Jg^{-1}. This behaviour might be associated with the heterogeneity of the surface since at first the adsorbate occupies more active sites than later and the generated heat for this effect is different and allows the confirmation of in which zone there is a greater adsorption.

Figure 1 is an interesting result of the given work which shows a variation of the immersion enthalpy in function of the amount adsorbed and the initial solution concentration, and shows that the intensity of the interaction changes in function of the liquid phase composition.

Figure 2 the relation between the adsorption capacity and the immersion enthalpies for a solution of monohydroxilated phenols with an initial concentration of 100 mg L^{-1} is shown with the purpose of establishing the effect of the pH; the highest immersion enthalpies are produced on a pH of 9 rather than pH 7, which is related with energetic interactions carried out on the surface of the solid and the adsorbate molecule, since at these conditions of pH non dissociated species prevail with presence of the monobasic anionic form for the three adsorbates, see Table 1, where the dispersive interactions and attractive electrostatic interactions intervene modifying the energetic interaction.

Resides, it is observed on Fig. 2 that at a pH of 11 the lowest values of immersion enthalpies are presented, in solution at this pH the anionic species prevail and less appropriate conditions for the adsorption are presented probably because the surface of the carbon is negatively charged ($pH > pH_{PZC}$ see Table 3) and repulsive electrostatic interactions intervene. On the other hand, a clear tendency of the immersion enthalpy in function of the pH is observed, for example, $-\Delta H_{inm}$ of 35.7; 30.8 and 24.6 Jg^{-1} for catechol, resorcinol and hydroquinone, respectively, at pH 7, for which it is possible to establish an order in the enthalpic contribution of the adsorption for phenolic compounds in correspondence with the hydroxyl group as follows: catechol > resorcinol > hydroquinone.

The immersion enthalpies were determined in the same way as the modified activated carbons by the reductive and oxidative treatment, with a pH of 7 for an initial concentration of 1,500 mg L^{-1}, corresponding to the maximum concentration used in the practice that presents the highest values of immersion enthalpies. On Fig. 3 an increase in the energetic interactions in the CAR produced between the adsorbate molecules and the surface of the solid is

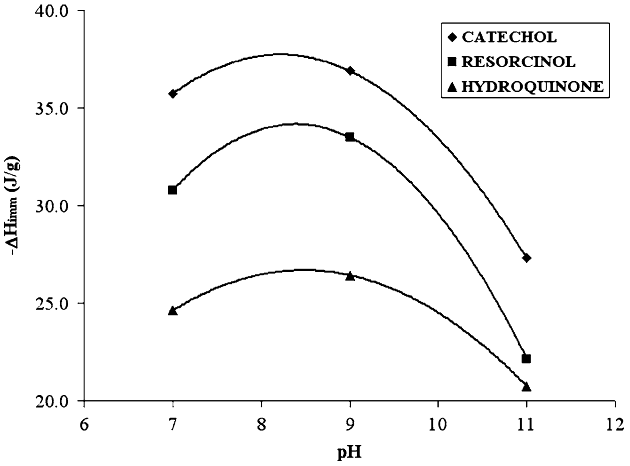

Fig. 2 Immersion enthalpies of CAG at different pH for different phenols

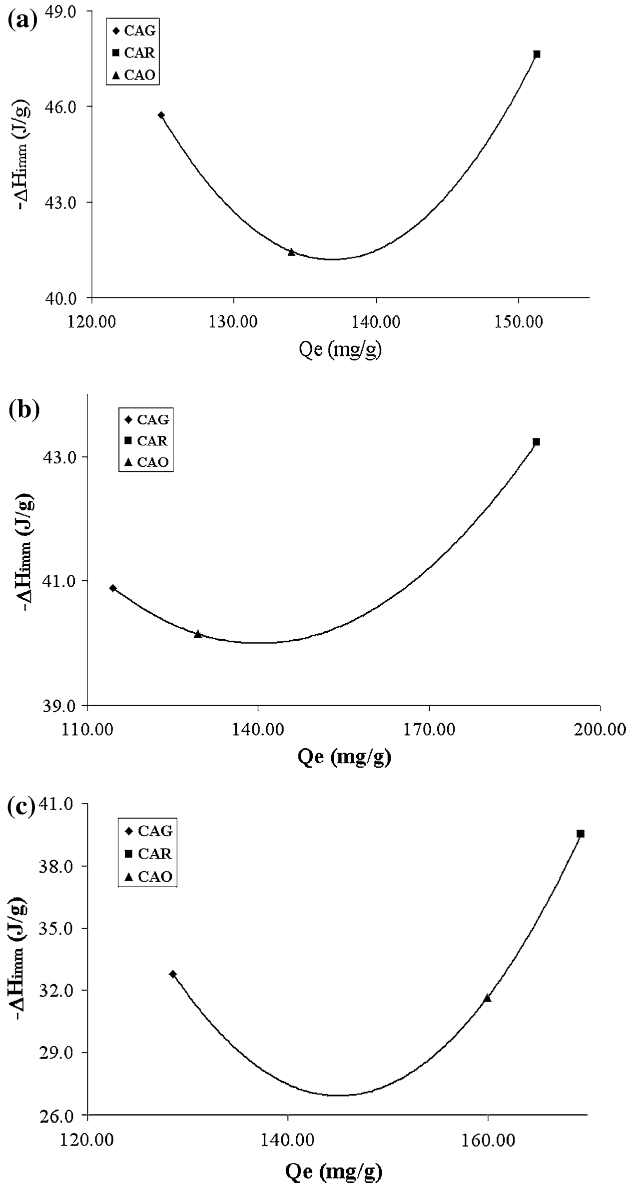

Fig. 3 Immersion enthalpies of carbons in function of phenols adsorbed quantity at pH 7. **a** Catechol; **b** Resorcinol and **c** Hydroquinone

observed, effect basically due to chemical surface which gives evidence of the nature of the possible adsorption sites.

The CAR sample presents an increase in the immersion enthalpies; all of the compounds are in molecular form, that is, in the process of adsorption the dispersive interactions mainly intervene. Because this sample has a basic character (pH_{PZC} 10.1), and consequently a low concentration of acid oxygenated functional groups (specially carboxylic, Table 3), the energetic interactions assumed are basically produced with π electrons of the grafeno layers, intensified for catechol, followed by resorcinol and hydroquinone 47.6; 43.2 and 39.5 Jg^{-1}, respectively.

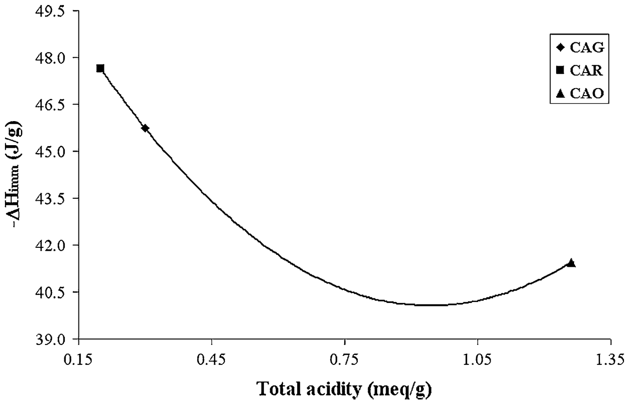

Fig. 4 Relation between immersion enthalpies in a resorcinol solution of 1,500 mg L^{-1} and the total acidity

On the CAO sample, Fig. 3a–b and c, a small decrease is appreciable in the immersion enthalpies for the CAO compared with CAG for the catechol case 41.4 and 45.7 Jg^{-1}, respectively. The results are similar; nevertheless it turns out interesting to appreciate the tendencies that complement the information obtained in the isotherm. The monohydroxilated phenols are found to be in a molecular or protonic form, for which there will be predominance for the electrostatic interactions since the surface of the solid is negatively charged (pH_{PZC} 4.3 see Table 2). In this specific case it is important to take in consideration that this sample has a high phenolic and carboxylic group concentration, which withdraw electronic density from the grafeno layers and therefore weaken the interactions between π electrons, which modify the energetic interactions.

Correlations can be made with the given results between the effect the position of the functional group, $-OH^-$, has in the molecule, since it causes a modification in the immersion enthalpy given that the interaction of each solute is different for each activated carbon. This is, for example, on Fig. 4, the immersion enthalpy is shown for a 1,500 mg L^{-1} solution of resorcinol at pH 7, in function of the total acidity of the carbonaceous samples; it is appreciated that at a higher acidity, the values of the immersion enthalpy will be lower, which is related with a smaller adsorption capacity, a result of the carboxylic groups that withdraw electronic density from the grafeno layers, decreasing the interaction with the adsorbate.

Figure 5, an enthalpic contribution of the position of the functional group $-OH^-$ is shown, comparing the interactions present in the monohydroxilated phenols for an initial concentration of 100 mg L^{-1} with the CAG sample. In this Figure it is appreciated that the *o*-hidroxyphenol or catechol presents a higher contribution, followed by the *m*-hidroxyphenol or resorcinol and *p*-hidroxyphenol or hydroquinone, 461.7; 380.6 and 338.0 $kJmol^{-1}$, respectively.

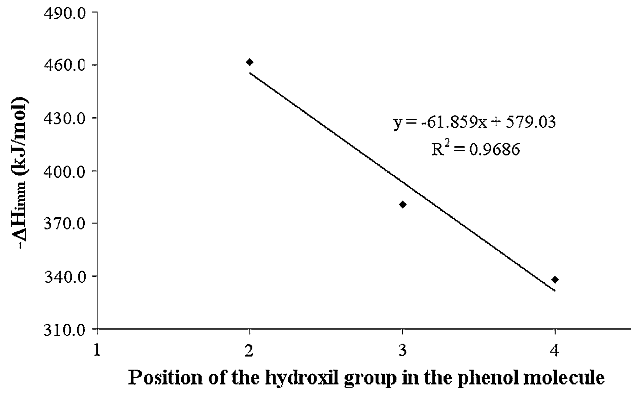

Fig. 5 Immersion enthalpies in function of the hydroxyl group position for the CAG

Finally, the –OH^{-} group enthalpic contribution, in which the difference is the position in the aromatic ring 2, 3 and 4, ortho, meta and para respectively, a linear relation is found where the slope is 61.9 kJmol^{-1} corresponding to the enthalpic decrees in the adsorption process for each phenolic compound studied and that benefits the catechol adsorption.

Conclusions

The values of the immersion enthalpies increase with the adsorbed amount for the three adsorbates, that is for example, for the catechol the immersion enthalpy increases with the retained amount from 21.5 to 45.7 Jg^{-1}.

The immersion enthalpies present the following arrangement: catechol > resorcinol > hydroquinone, with the values $-\Delta H_{inm}$ of 35.7; 30.8 and 24.6 Jg^{-1} respectively at pH 7 for monohydroxilated phenol solutions of 100 mgL^{-1}.

The immersion enthalpies for a catechol solution of 1,500 mg L^{-1}, with values of 47.6; 45.7 and 41.4 Jg^{-1} para el CAR, CAG and CAO, respectively, point out a higher interaction with the activated carbon CAR that presents a lowest total acidity with 0.20; 0.30 and 1.26 meq g^{-1} for CAR, CAG and CAO, respectively.

The enthalpic contribution in agreement with the position of the hydroxyl group on the aromatic ring is 61.9 kJmol^{-1}.

The results show a variation in the immersion enthalpy in function of the amount adsorbed and the initial concentration of the solution, which allows seeing that the intensity of the interaction changes in function of the liquid phase composition.

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