



Effect of the pH in the adsorption and in the immersion enthalpy of monohydroxylated phenols from aqueous solutions on activated carbons

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ABSTRACT

An activated carbon CarbochemTM – PS230 was modified by chemical and thermal treatment in flow of H₂ in order to evaluate the influence of the activated carbon chemical surface in the adsorption of the monohydroxylated phenols. The solid-solution interaction was determined by analyzing the adsorption isotherms at 298 K at pH 7, 9 and 11 during 48 h. The adsorption capacity of activated carbons increases when the pH solution decreases. The amount adsorbed increases in the reduced carbon at the maximum adsorption pH and decreases in the oxidized carbon. In the sample of granulated activated carbon, CAG, the monohydroxylated phenols adsorption capacity diminishes in the following order catechol > hydroquinone > resorcinol, at the three pH values. The experimental data are evaluated with Freundlich's and Langmuir's models.

The immersion enthalpies are determined and increase with the retained amount, ranging between 21.5 and 45.7 J g⁻¹. In addition, the immersion enthalpies show more interaction with the reduced activated carbon that has lower total acidity contents.

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1. Introduction

Phenol and its derivatives are raw materials in the chemical industry and as a result, they are widely found in its effluents. Therefore, its presence is more and more frequent in the bodies of water and due to its high toxicity, high oxygen demand and low biodegradability, the phenolic compounds are considered high-priority polluting agents in waste water treatment [1–5].

The extended use of activated carbons as adsorbent of inorganic and organic polluting agents in the water is due to both its texture and the chemical properties of the surface, which also depend on the original materials and the method used to prepare the carbonaceous solid, which can be modified with physical and chemical treatments to improve the adsorbent properties. The factors which influence the adsorption process in the solution include the activated carbon, the adsorbate, the chemist who prepared the solution and its temperature [5–7].

The immersion enthalpies of activated carbon in different solutions provide a way to directly measure the energy involved in the process, that is, the energy related to the surface area exposed to the liquid and the specific interaction between the solid surface and the immersion liquid. This is established as a thermodynamic property that characterizes the solid–liquid interaction [8–12].

This work analyzes the adsorption of three monohydroxylated phenols, catechol, resorcinol and hydroquinone [13–14]. The adsorption isotherms of phenols are determined in three activated carbons samples: granulate activated carbon, CAG; modified chemically by oxidation with a solution of HNO₃, CAO; and thermally in H₂ flow, CAR. Other aspects reviewed include the effect of the monohydroxylated phenol solutions at different pH values (7, 9 and 11) and the influence of the chemical surface of activated carbons and the pH solution value in the immersion enthalpy of activated carbons in aqueous solutions of different phenols concentrations.

2. Experimental

A granulated activated carbon CarbochemTM – PS230 is used for this experiment. The precursor of this carbon is coconut shell.

2.1. Modification of the granulated activated carbon

2.1.1. Hydrogen atmosphere heat treatment

About 20 g of granulated activated carbon are placed in the reducing system with hydrogen. Temperature is increased to 393 K; vacuum is set to about 10⁻⁴ mmHg. Later the hydrogen is introduced. In these conditions, the oven is warmed progressively to 573 K during 6 days. Finally the activated carbon is stored in a nitrogen atmosphere

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Table 1
Important properties of monohydroxylated phenols [18].

Adsorbate	Catechol	Resorcinol	Hydroquinone
pKa	9.3–13.0	9.4–12.3	10.0–12.0
Solubility (g/100 g H ₂ O) 298 K	45	123	8

2.1.2. Treatment with nitric acid

Six grams of the granulated activated carbon are placed with a 7 mol L⁻¹ nitric acid solution in soxhlet equipment for 9 h at the solution boiling temperature, using 60 mL of acid per gram of activated carbon. The sample is then washed with distilled water until a constant pH value is obtained and the activated carbon then dried at 383 K for 24 h. Finally the samples are stored in a closed container in nitrogen atmosphere

2.2. Textural and chemical analysis of the original and modified activated carbons

The carbonaceous samples, about 0.100 g, are degassing at 523 K for a period of 3 h in an Autosorb 3B, Quantachrome Co. The corresponding adsorption nitrogen isotherms are obtained with this apparatus at 77 K. In addition, the acid and basic sites are determined by the Boehm [15] acid–base titration method and the point of zero charge is determined by the mass titration method [16].

2.3. Adsorption in the aqueous phase

Table 1 presents the pKa and solubility of the adsorbates. Monohydroxylated phenols concentration in aqueous solution is determined by a UV spectrophotometric method. The maximum absorbance wavelength is determined at pH values of 7, 9 and 11 in a Thermospectronic Genesys 10.

The adsorption isotherms data are obtained by putting 0.500–0.250 g of the carbonaceous samples in contact with a 50 mL volume of monohydroxylated phenols solutions at known initial concentrations ranging from 20 to 2000 mg L⁻¹, with pH adjustment at 298 K for 48 h.

2.4. Immersion Calorimetry

2.4.1. Determining immersion enthalpy

Phenolic solutions: 50.0 mL of aqueous solutions of phenolic compounds at pH 7, at concentrations ranging from 20 to 1500 mg L⁻¹ are placed in the calorimetric cell and between 0.500 and 0.250 g of the carbonaceous samples are weighed in a glass cell; the cell is assembled and allowed to equilibrate for approximately 40 min. When the variation of the exit electrical resistance thermistor is constant, the readings start at an initial period of 15 min, with resistance readings every 20 s; then the activated carbon samples are put in contact with the phenolic compounds solutions, the resistance readings are continued until they remain constant and finally, the system is electrically calibrated [17]. The heat amount for the process examined is equal to $Q = C_p \Delta T_{\text{corrected}}$; where C_p is the calorific capacity of the system studied plus the calorific capacity of the cell, $\Delta T_{\text{corrected}}$ is the temperature difference for which a graphic correction is made because of the small but existing heat leak [18]

Table 2
Textural and chemical characteristics of the activated carbons.

Simple	Surface area BET (m ² g ⁻¹)	Volume micropore (cm ³ g ⁻¹)	Volume mesopore (cm ³ g ⁻¹)	Total acidity (meq g ⁻¹)	Total basicity (meq g ⁻¹)	pH _{PZC}
CAG	1140	0.51	0.12	0.30	0.60	9.8
CAR	1171	0.56	0.12	0.20	0.61	10.1
CAO	1181	0.56	0.09	1.26	0.25	4.3

Water: The immersion enthalpy measurements of the carbonaceous material are taken in distilled water at pH 7, in the same way as for the previous procedure.

3. Results and discussion

3.1. Activated carbon properties

The physical and chemical characteristics of the activated carbons studied in this work are shown in Table 2. The Table displays the values for the micropore and mesopore volume obtained by the Dubinin–Raduskevich's method. The results show that the oxidation and reduction treatments done in the activated carbon do not produce any significant changes in the textural characteristics of carbonaceous materials, but if produce changes in the chemical properties of the surface. The activated carbons used have similar characteristics to the others research with phenol [19].

3.2. Adsorption from solution

3.2.1. Effect of solution pH on monohydroxylated phenols adsorption

The adsorption of catechol and hydroquinone on granulated activated carbon, CAG, is observed in function of the pH solution in respective isotherms, Fig. 1, for pH values of 7, 9 and 11. This is done in order to evaluate the system behavior at pH values near the monohydroxylated phenols pKa values.

This Figure shows that as the pH solution increases from 7 to 11, the amount of the phenols adsorbed diminishes. This indicates that adsorption is increased when the protonated species of phenols are present. The isotherms data exhibited on Fig. 1 do not follow the behavior of the Langmuir model because the mass of the adsorbed phenols, in an ample rank of concentrations like the one considered in this work, 20 to 2000 mg L⁻¹, does not become asymptotic at high concentrations, but continues increasing when the concentration rises. For this reason, the Langmuir model doesn't interpret the data of the isotherm correctly.

Based on the above, it could be said that monohydroxylated phenols adsorption is not due to a single mechanism; instead, it is based on several types of interactions between the species present in the solution and the surface of the activated carbon, as well as the pH solution. At pHs lower than 9.8 corresponding to pH_{PZC} of the CAG sample, the surface activated carbon is loaded positively, and the species adsorbed at pH 7 are the protonated that are neutral molecules. In these conditions, the dispersive interactions determine the adsorption process.

At pH 9, the adsorption isotherms show linear behavior at concentrations below than 200 mg L⁻¹ and later, the quantity retained increases slightly. The adsorbed species are the protonated and monobasic anionic and due to the positive charge of the carbon surface, attractive and dispersive electrostatic forces begin to interact between the surface and the anion, favoring their accumulation.

At pH 11, the surface is loaded negatively, the pH value is more than pH_{PZC} and the species present are the anionic monohydroxylated phenols. Therefore, the anionic species present in the solution repulse the surface activated carbon. The adsorption occurs when the repulsive electrostatic forces win, and the adsorption at low

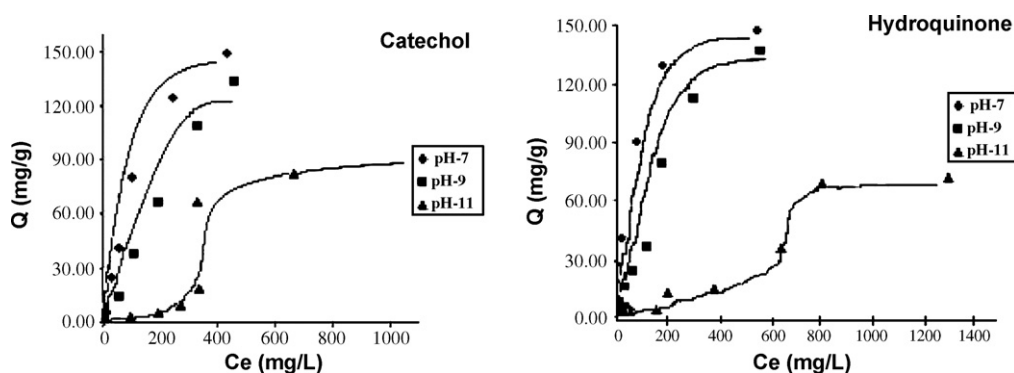


Fig. 1. Monohydroxylated phenols adsorption isotherms on the CAG sample in function of the pH solutions.

concentrations is less than at high concentrations, as show in the adsorption isotherms.

In general terms, in the adsorption of the three adsorbates, the pH significantly affects the adsorption of the monohydroxylated phenols on the activated carbon. This is more evident in basic conditions since the adsorption capacity diminishes when the pH in increased. The effect of pH upon adsorption of phenolic compounds has been observed and related by various authors [20–24] to the degree of ionization of the phenolic adsorbate.

The electronic density of the aromatic ring is strongly affected by the nature of its functional groups. A hydroxyl group acts as an electron donor group, resulting in a high electronic density in the aromatic ring π system. In these conditions, the dispersive interactions of π – π type are increased with the number of hydroxyls and its position in the aromatic ring [25–27].

The difference in the quantity retained depends on the solubility, the adsorbate polarity and the hydroxyl group position in the aromatic ring. Resorcinol solubility in water is much greater than that of catechol and hydroquinone, which means that resorcinol has a strong affinity with water. Perhaps this is one of the reasons for the lower resorcinol adsorption. In addition, the difference of the acidity of the monohydroxylated phenols due to contributions of the phenoxide ion resonance structures – which in this case are greater for phenol with the hydroxyl group in ortho position followed by meta and para positions – affects the interaction between the activated carbon and the adsorbate as observed in terms of isotherms. Thus, there is major interaction between the catechol and the activated carbon: the effects of solubility and the hydroxyl group position increase the adsorption capacity for catechol, followed by hydroquinone and for resorcinol. A work with polymeric resins [28] shows that the adsorption of catechol is larger than resorcinol, as in this study, revealing the greater interaction between the adsorbent and catechol.

3.2.2. Effect of chemical surface on monohydroxylated phenols adsorption

In order to evaluate the reduction and oxidation of the activated carbon surface in the adsorption of monohydroxylated phenols, the isotherms of samples CAG, CAR and CAO are determined. Fig. 2 shows the resorcinol isotherms on activated carbons at pH 7.

The reductive treatment diminishes the total acidity 1.3 times with respect to CAG. Therefore, it is expected that the concentration of π -electrons increases in the graphene layers, meaning that there is an attraction between the π -electrons of the activated carbon basal planes and the aromatic ring electronic density of monohydroxylated phenols [29]. Because the pH solution is less than pH_{PZC} , only dispersive forces are acting in this interaction. Nevskaja et al. [30] report that the specific adsorption capacity increases considerably when the surface groups are eliminated, in agreement with other studies on oxidized activated carbons [31].

The oxidation increases the quantity of acid groups that retire the electronic density of the graphene layers, thus diminishing the amount of adsorbed solute. This way, a main number of superficial oxygen groups increases the water affinity, which would explain the lower amount of retained solute [32,33].

3.2.3. Adsorption isotherms

The experimental data of adsorption isotherms are fitted with Freundlich and Langmuir models. Deviation percentage are calculated as follows: $\% \text{Desv} = 1/N \sum |q_{\text{cal}} - q_{\text{exp}}/q_{\text{exp}}| \times 100$, where N = number of experimental data [7].

Table 3 summarizes the resulting linearization parameters for the adsorption data applying the Freundlich and Langmuir modes. In general, if the kf value is analyzed, this is an indication of the adsorption capacity, which is greater for the solution at pH 7 in the CAG. The capacity decreases as follows: it is greater for pH 7, followed by pH 9 and finally pH 11, with kf values of 2.17; 0.15 and $0.07 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$.

The value of $1/n$ is a measurement of the surface heterogeneity. A value near 0 indicates a heterogeneous surface [4]. When the value of $1/n$ is less than 1, then the adsorption process is favorable, again, for CAG, in the case of a pH 7 solution, the adsorption is more favorable than for the other solutions (pH 9 and 11). The percentage of deviation of the model is greater for pH 11 than for the other pH values, which again shows the reduction of the adsorption process at this pH for the three adsorbates.

Perhaps the most important parameter to compare is the $Q_{\text{máx}}$ value of the Langmuir model, because this measures the adsorption capacity of the adsorbate. Table 4 presents the results obtained for the model mentioned. By comparing the results of the mono-

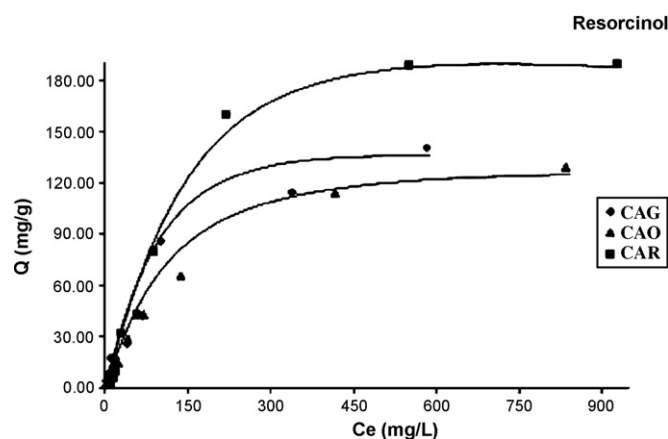


Fig. 2. Resorcinol adsorption isotherms on activated carbons CAG, CAR and CAO at pH 7.

Table 3
Parameter values of the Langmuir and Freundlich models for the monohydroxylated phenols adsorption on the CAG.

Adsorbate	pH	Langmuir				Freundlich			
		$Q_{\text{máx}}$ (mg g ⁻¹)	K (L mg ⁻¹)	R^2	%Des	kf (mg ^{1-1/n} L ^{1/n} g ⁻¹)	1/n	R^2	%Desv
Catechol	7	238.10	4.2E-3	0.90	0.21	1.49	0.81	0.96	3.15
	9	nf	nf	nf	nf	0.49	0.94	0.97	2.47
	11	nf	nf	nf	nf	nf	nf	nf	nf
Resorcinol	7	178.57	6.0E-3	0.94	0.51	2.17	0.70	0.95	3.41
	9	156.25	3.2E-3	0.94	0.40	1.15	0.72	0.95	3.51
	11	44.25	1.7E-3	0.93	1.00	0.07	0.88	0.81	16.33
Hydroquinone	7	169.49	1.3E-2	0.99	2.44	2.15	0.76	0.84	13.97
	9	nf	nf	nf	nf	0.21	1.08	0.91	7.77
	11	nf	nf	n	nf	0.05	1.01	0.92	7.77

nf: not fit.

Table 4
Parameter values of the Langmuir and Freundlich models for the monohydroxylated phenols adsorption on the CAG and carbons modified at pH 7.

Adsorbate	Sample	Langmuir				Freundlich			
		$Q_{\text{máx}}$ (mg g ⁻¹)	K (L mg ⁻¹)	R^2	%Des	kf (mg ^{1-1/n} L ^{1/n} g ⁻¹)	1/n	R^2	%Desv
Catechol	CAG	238.10	4.2E-3	0.90	0.21	1.49	0.81	0.96	3.15
	CAR	181.82	5.7E-3	0.97	3.61	1.39	0.74	0.87	8.58
	CAO	178.57	3.9E-3	0.97	0.09	1.62	0.70	0.96	1.79
Resorcinol	CAG	178.57	6.0E-3	0.94	0.51	2.70	0.70	0.95	3.41
	CAR	232.56	5.5E-3	0.97	1.72	2.00	0.73	0.89	6.61
	CAO	163.93	4.8E-3	1.00	0.73	2.09	0.66	0.97	1.67
Hydroquinone	CAG	169.49	1.3E-2	0.99	2.44	2.15	0.76	0.84	13.97
	CAR	232.56	8.3E-3	0.97	4.60	3.98	0.62	0.84	10.73
	CAO	232.56	3.2E-3	0.80	0.94	2.27	0.63	0.87	9.23

hydroxylated phenols adsorption at pH 7, which is the pH that is best adapted to this model, the $Q_{\text{máx}}$ value is clearly greater for catechol, followed by resorcinol and hydroquinone.

Comparing the results for resorcinol adsorption, it can be observed that based on the pH for CAG, the $Q_{\text{máx}}$ value diminishes as the pH increases, 178.57; 156.25 and 44.25 mg g⁻¹, at pH 7, 9 and 11, respectively. In the case of the K value (which measures the adsorbent affinity by solute molecules), the K value decreases while pH increases as can be seen on Table 4 for resorcinol: 6.0 E-3; 3.2E-3 and 1.7E-3 L mg⁻¹, at pH 7, 9 and 11, respectively.

Table 4 presents the linearization parameter results of adsorption data for the original and the modified activated carbons when the Freundlich and Langmuir models are applied. According to the values obtained for the kf constant, adsorption occurs in the following order: it is greater for the oxidized activated carbon, CAO, less for the granulated activated carbon, CAG, and lowest for the reduced activated carbon, CAR. This is not what occurs for the adsorption isotherms.

In the case of the maximum quantity adsorbed, $Q_{\text{máx}}$, of the Langmuir model, the superficial chemical modifications affect the $Q_{\text{máx}}$ value, so that it is greatest for CAR, than for CAG and CAO. When the hydroquinone is the adsorbate, the order changes, with values of 232.56; 232.56 and 169.49 mg g⁻¹ for CAR, CAO and CAG, respectively. For catechol, the order is 238.10; 181.82 and 178.57 mg g⁻¹ for CAG, CAR and CAO, respectively [34].

3.3. Immersion calorimetry

Fig. 3 presents the results obtained for the immersion enthalpy, $-\Delta H_{\text{imm}}$, at pH 7, in function of the quantity of monohydroxylated phenols adsorbed in the granular activated carbon, CAG. Differences can be observed in the value of the immersion enthalpy at small magnitudes; at pH 7, the protonated species of the monohydroxylated phenols predominate and mainly dispersive interactions occur.

In addition, as shown on Fig. 3, the immersion enthalpy increases with the adsorbed amount, and becomes asymptotic when the quantity retained is greater. This is because the surface has been saturated with the adsorbate. For example, the immersion enthalpy for catechol increases with the amount retained from 21.5 to 45.7 J g⁻¹ [35].

The immersion enthalpy for the CAG sample in water at pH 7 was 16.6 ± 0.8 J g⁻¹, value smaller que el obtenido por Stoeckli et al. [36], however to evaluate the interactions that occur, the solvent effect was also considered because is important to take into account that the influence of the species which compete for the adsorption places in solution depend not only on the pH, but also on the adsorbate molecule pKa and of the activated carbon pH_{PZC}. The full effect is interesting to evaluate [10,37].

3.3.1. Effect of solution pH on immersion enthalpy

Fig. 4 shows the relation between the immersion enthalpies of activated carbon CAG in a solution with an initial concentration of

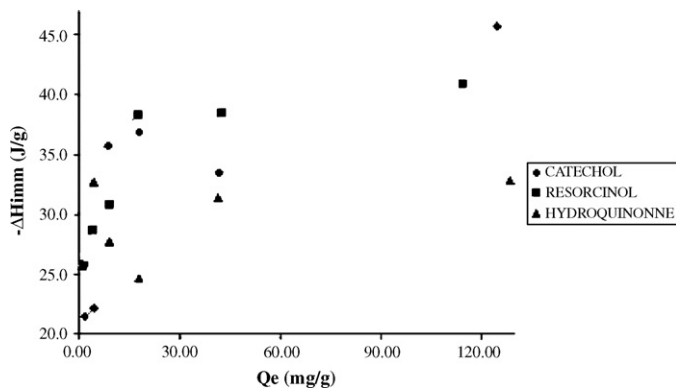


Fig. 3. Immersion enthalpies of CAG in function of quantity phenols adsorbed at pH 7.

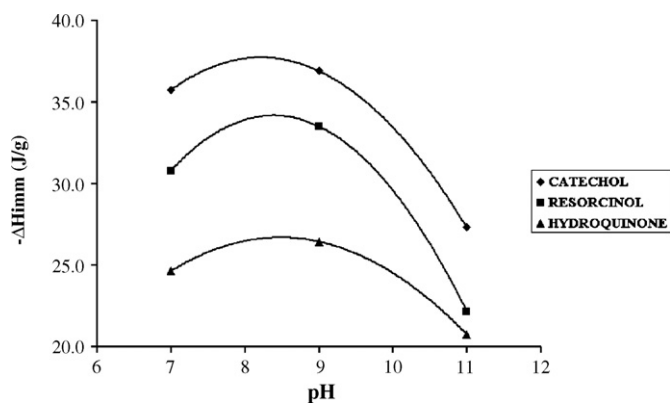


Fig. 4. Immersion enthalpies of CAG at different pH for phenols.

100 mg L⁻¹ for the monohydroxylated phenols and pH; values are higher for the immersion enthalpy at pH 9 than at pH 7 and the difference is owed to the energetic interactions produced on the solid surface and the species present in the solution. This is because at these pH levels, the non-dissociated species predominate, although the monobasic anionic forms are present for the three adsorbates. For this reason, dispersive and electrostatic interactions will occur to modify the energetic interaction.

In addition, Fig. 4 shows that at pH 11, lower values of immersion enthalpy appear. For this level of pH, the anionic species predominate and the conditions are less suitable for the adsorption, probably because the surface of the activated carbon is loaded negatively and repulsive electrostatic interactions will occur. On the other hand, immersion enthalpies of $-\Delta H_{\text{imm}}$, of 35.7; 30.8 and 24.6 J g⁻¹ are obtained for the catechol, resorcinol and hydroquinone, respectively at pH 7, which establish an order in the enthalpic contribution of the phenolic compounds adsorption according to the position of the hydroxyl group: catechol is greater than resorcinol and resorcinol is greater than hydroquinone. Kumar et al. [38] study the adsorption of resorcinol and catechol on granular activated carbon, in this work catechol is adsorbed to a greater extent than resorcinol.

3.3.2. Effect of chemical surface on immersion enthalpy

Finally, the results obtained show correlations between the position effect of the $-\text{OH}^-$ functional group in the molecule, since this group leads to a modification in the immersion enthalpy as a result of the different interaction of each solute with the activated carbon. Fig. 5 shows the immersion enthalpy for a resorcinol

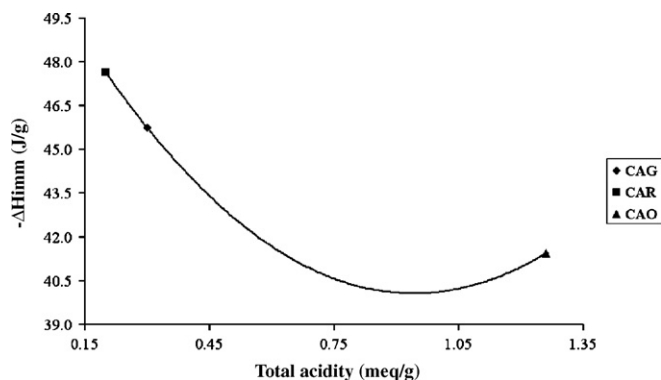


Fig. 5. Relation between immersion enthalpies in resorcinol solution of 1500 mg L⁻¹ and the total acidity.

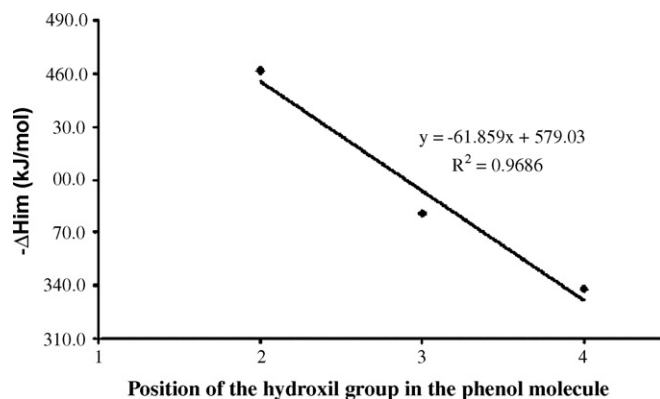


Fig. 6. Immersion enthalpies in function of the hydroxyl group position for the CAG.

solution of 1500 mg L⁻¹ at pH 7, as a function of the carbonaceous samples total acidity; as acidity increases, the immersion enthalpy increases, which is related to a lower adsorption capacity, product of the carboxylic groups that retire electronic density of the graphene layers. The interaction with the adsorbate then decreases.

Fig. 6 shows the enthalpic contribution of the $-\text{OH}^-$ functional group position when the interactions of the monohydroxylated phenols at an initial concentration of 100 mg L⁻¹ are compared with the CAG sample. In this Figure, it can be seen that the catechol has the greatest contribution, followed by resorcinol and hydroquinone, 461.7; 380.6 and 338.0 kJ mol⁻¹, respectively.

Regarding the enthalpic contribution of the $-\text{OH}^-$ group, in which the change is constituted by the position in the aromatic ring, 2, 3 and 4 (ortho, meta and para respectively), there is a linear relation with a slope of $-61.9 \text{ kJ mol}^{-1}$, which corresponds to the enthalpic diminution in the process of adsorption for each phenolic compound that has been studied and which favors the adsorption for the catechol.

4. Conclusions

The capacity of granulated activated carbon to adsorb monohydroxylated phenols catechol, resorcinol and hydroquinone depends on the pH of the solution; the quantities adsorbed in accordance with the adsorption isotherms decrease when the pH is increased from 7 to 11 and the maximum adsorption is obtained at pH 7.

The chemical modifications, oxidation and reduction on the surface of the activated carbon increase the adsorption capacity in CAR and decrease in CAO.

The values of the immersion enthalpies increase with the quantity adsorbed of phenols for pH 7, in which one obtains the maximum adsorption chosen of the isotherms.

The enthalpic contribution according to the position of the hydroxyl group in the aromatic ring is $-61.9 \text{ kJ mol}^{-1}$.

The results show a variation in immersion enthalpy, based on the quantity adsorbed and on the initial concentration of the solution, similar to what occurs in the adsorption isotherms and which allow for the conclusion that the intensity of the interaction changes in function of the liquid phase composition.

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