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Application of the Sips model to the calculation of maximum adsorption capacity and immersion enthalpy of phenol aqueous solutions on activated carbons

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ABSTRACT

The Sips model for heterogeneous systems was used to describe the immersion enthalpy, maximum adsorption capacity at three temperatures, namely, 283, 291 and 308 K; and interactions between phenol aqueous solutions and activated carbon modified on its surfaces by impregnation with 6.0 M HNO_3 and 3.0 M H_3PO_4 solutions. Activated carbon properties, such as porosity, Brunauer-Emmett-Teller (BET) surface area and volume and size pore distributions, were determined using N_2 adsorption at 77 K. Surface area values were calculated to be between 469 and 864 m^2/g. Also, the pH at the point of zero charge, acidity and total basicity for the activated carbons were obtained. The result showed that the Sips model in addition to describe the phenol concentration in equilibrium can be used to study immersion enthalpy when $1/n_s$ is equal to 1.

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1. Introduction

Phenol is a raw material present in many everyday products. For example, it is used in refinery effluents, paper production, resins and ink production [1]. The treatment of wastewater containing phenol is very important because it is dangerous to aquatic organisms and can produce a bad taste and odor even at low concentrations [2]. The adsorption of phenolic residues on activated carbons has been developed as an effective technology to combat this issue [3].

The adsorption process of phenol from aqueous solution on activated carbon depends on variables such as the activated carbon surface area, the functional groups on its surface and their load, the pH of the solution and the interactions between ions, among other factors [4,5].

The determination of adsorption isotherms from aqueous solution is one way to analyze the interactions of phenol on activated carbon. The interactions can be described by different mathematical models. Many authors use the Freundlich and Langmuir equations, which contain empirical parameters [5]. A model was developed by Sips in 1948 to calculate the distribution of site adsorption energies on catalyst surfaces from adsorption isotherms [6]. This model has also been used to study adsorption on activated carbons with good results. The Sips equation has three parameters and it combines the Freundlich and Langmuir equations [7,8]. The equation is written as:

$$q_e = \frac{q_{ms}.K_s.C_e}{1+K_s.C_e^{1/n_s}} \tag{1}$$

where q_e (mmol/g) is the amount adsorbed at equilibrium, q_{ms} (mmol/g) is the Sips maximum adsorption capacity, C_e (mmol/L) is the adsorbate concentration at equilibrium, K_S (L/mmol) is the Sips equilibrium constant for heterogeneous solids and n_s is the heterogeneity parameter [8].

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The difference between the Sips and Langmuir equations lies in the additional parameter n_s. This can be considered as a parameter that characterizes the system's heterogeneity and it come from either adsorbent or adsorbate or a combination of both. n_s is generally greater than unity and the system is more heterogeneous when the value is larger. In the Sips equation, it can be observed that when $1/n_s$ is 1, it reduces to the Langmuir equation, and when $K_S.C_e^{1/ns}$ is far less than 1, it becomes the Freundlich equation [7,9]. Thus, the Sips equation can describe solute adsorption processes in a wide range of concentrations.

Immersion enthalpy is another method that can be used to analyze the phenol adsorption process from aqueous solutions on activated carbons. The adsorption process involves energy transfer as heat between the system and its environment, and it is associated with forming an adsorbed layer. It not only depends on the available surface area of the activated carbon, but also specific interactions between groups present on its surface and the immersion liquid. The immersion enthalpy, ΔH_{inm} (J/g), is defined as the energy transferred as heat at constant temperature and pressure, which occurs when a solid is immersed in a liquid [10,11].

This study illustrates the use of immersion calorimetry and adsorption from aqueous solutions to examine the behavior of phenol from aqueous solution-activated carbons with modified surface interactions. The Sips model is used to calculate the maximum adsorption capacity and describe the immersion enthalpy.

2. Experimental

2.1. Preparation of activated carbons

An activated carbon produced from coconut shell was modified to obtain two activated carbons by impregnation with 6.0 M HNO_3 and 3.0 M H_3PO_4 solutions. The preparation of this activated carbon has been described in previous works [12,13].

2.2. Sample identification

Sample identification was realized using a code of two letters. The first corresponds to granular activated carbon (G) and the second corresponds to impregnation-type realized nitric acid (GN) and phosphoric acid (GP).

2.3. Activated carbon characterization

The textural properties of the activated carbons were calculated from N_2 adsorption isotherms at 77 K, obtained using sortometer IQ 2 equipment (Quantachrome). The surface area (S) was obtained using the Brunauer-Emmett-Teller (BET) model. The micropore volume (Vo) was found by applying the Dubinin-Astakhov model. The total volume of pore (V_T) and pore size distribution were obtained using density functional theory (DFT). Finally, the mesopore volume (V_m) was calculated using the difference between the total and micropore volumes [14].

The acidic and basic groups on the activated carbon surface were calculated through acid-base titration using a modified Boehm method [15]. Acidic groups were determined in a flask series with about 0.4 g of activated carbon in each one. A total of three series were prepared, one for each activated carbon obtained. Then, to each flask was added 50 mL of 0.1 M NaOH solution, samples were then stirred for 5 days at 291 K. Finally, they were titrated with a 0.1 M HCl solution. To determine the basic groups, the same method was used, but in this case, 50 mL of 0.1 M HCl solution was added and the 0.1 M NaOH solution was used for titration.

The pH at the point of zero charge (pH_{PZC}) was determined by a mass titration method proposed by Noh and Scharz [16,17]. Activated carbon between 0.01 and 0.60 g were weighed in a flask series (one series for each activated carbon sample), and to each flask was added 10 mL of 0.1 M NaCl solution. These samples were stirred for 48 h at 291 K and finally, equilibrium pH values were determined.

2.4. Adsorption of phenol from aqueous solution

A volume of 50 mL of phenol solution between 20 and 1000 mg/L was added into a flask resealable series that contained around 0.1 g of activated carbon (one series for each activated carbon sample). Flasks were stored at constant temperature for 15 days to ensure equilibrium conditions. Then, the samples were filtered and solution concentrations in equilibrium were determined by UV spectroscopy with Thermo Spectronic Genesys 5 equipment at a λ_{max} of 268 nm. To evaluate the temperature effect on the activated carbon adsorption capacity, isotherms were built at three different temperatures of 283, 291 and 308 K.

The amount of phenol adsorbed in equilibrium q_e (mmol/g) was calculated using the Equation 2.

$$q_e = V.\frac{C_o - C_e}{m} \tag{2}$$

where C_o (mmol/L) is the initial phenol concentration, C_e (mmol/L) is the final phenol concentration, V (L) is the solution volume and m (g) is the activated carbon weight.

2.5. Activated carbons: immersion enthalpy determination in phenol aqueous solutions

The immersion enthalpies of activated carbon-phenol solution systems were determined using phenol aqueous solutions between 20 and 1000 mg/L from immersion calorimetry. Measurements were carried out at 291 K in a heat conduction calorimeter built in our laboratory [18]. This equipment uses thermopiles of semiconductor materials as a thermal sensor and it is coupled to an aluminum block containing a stainless steel cell of 10 mL. Phenol solutions were placed into the cell as an immersion liquid. Once the system reached thermal equilibrium (about ± 3 μV), 0.1 g of activated carbon sample was immersed into the corresponding phenol solution. The electric potential continues to be recorded until a baseline occurs, indicating that thermal equilibrium has again been reached. Finally, applying a potential and a current known to a heating resistor contained in the cell immersion make electric calibration. The immersion enthalpy is obtained from the integration curve electrical potential versus time of the sample and its comparison with the calibration curve [18]. The equation to determine enthalpy, ΔH (J/g) from our results is

$$\Delta H_{inm} = \frac{V.I.A_{inm}}{m.A_{cal}} \tag{3}$$

where V (V) is the warming potential, I (A) is the amperage applied to the heating resistor at time t (s) during electric calibration, A_{inm} is the area under the curve corresponding to the energy transferred as heat during immersion and A_{cal} is the area under the curve produced during electrical calibration.

3. Results and discussion

3.1. Activated carbon characterization

Figure 1 shows the BET determination using the Equation (4). It was calculated from N_2 adsorption isotherms at 77 K for the original activated carbon, G, and the impregnated samples with nitric acid, GN, and phosphoric acid, GP.

Table 1. Activated carbon textural characterization obtained from N_2 adsorption isotherms at 77 K.

Sample	S_{BET} (m²/g)	C	Best E (kJ/mol)	Best n	Pore radius (nm)	V_o ^{a} (cm³/g)	V_{meso} ^{b} (cm³/g)	V_T ^{c} (cm³/g)
G	864	1729	8.3	2.1	0.84	0.33	0.02	0.35
GP	863	1287	7.7	2.2	0.71	0.33	0.04	0.37
GN	469	1149	7.4	2.1	0.72	0.18	0.04	0.21

^{a} Micropore volume and pore radius (values calculated from the Dubinin-Astakhov model).
^{b} Mesopore volume.
^{c} Total volume (DFT method-slit/cylindr. pores, QSDFT adsorption branch).

$$\frac{P/P_0}{(P_0-P)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} x \frac{P}{P_0} \tag{4}$$

Figure 1 shows that the fit to the BET model was realized for relative pressures of about 0.003 to 0.07. This range is below 0.05 to 0.35 proposed by Brunauer, Emmett and Teller [19]. The application of the BET equation must be limited to the range were [$V(1-P/P_0)$] continuously increases with P/P_0 according to ISO FDIS 9277 [20]. The results indicate that activated carbons are microporous; also it can be observed that the G and GP activated carbons overlap, while the GN activated carbon has a slope different from these. The results suggest that phosphoric acid treatment at 293 K does not significantly alter the textural properties of G, whereas treatment with nitric acid changes the activated carbon.

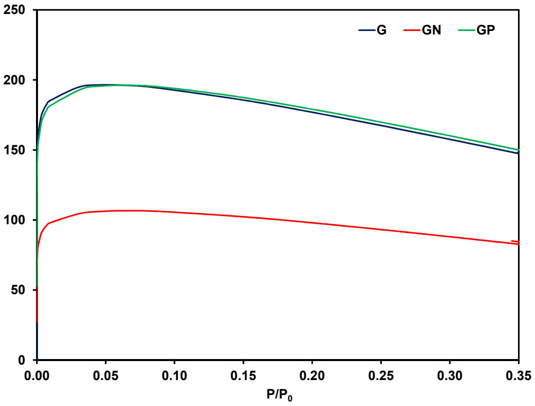

Figure 1. Plot of P/P_0 *vs* $V(1-(P/P_0))$ used to determine the upper limit for BET range.

Table 1 summarizes the activated carbon textural properties calculated from N_2 adsorption data at 77 K. The surface area was calculated using the BET [19] and Evich [21] model, micropore volume; V_o obtained by applying the Dubinin-Astakhov model, total pore volume, V_T was determined by DFT and mesopore volume, V_m, by the difference between total volume and micropore volume.

As shown in Table 1, the pore radius for all activated carbons is below 2 nm. According to IUPAC [22] classification, they correspond to microporous activated carbons. The results also show that impregnation of activated carbon with nitric acid solution produces a loss in activated carbon surface area of 54%. This is reflected by a decrease in micro-porosity and a small increase in meso-porosity. This behavior can be attributed to the oxidizing ability of nitric acid. Impregnation with phosphoric acid solution does not generate an increase or decrease in surface area or micro-porosity, although it is possible to observe a slight increase in meso-porosity for this activated carbon.

With regard to micropores, the heterogeneity given by the n term of the Dubinin-Astakhov equation shows that impregnations do not produce a change in this. The values obtained for n are around 2, this suggests that the micropore volumes for this activated carbons obtained by the Dubinin-Astakhov equation are equivalent to those obtained from the Dubinin-Radushkevich equation.

The E factor from the Dubinin-Astakhov equation is related to the micropore characteristic energy and decreases with impregnations in the order of G > GP > GN. By relating this result with phenol absorptions it can be observed that most absorption occurs in the opposite order of GN > GP > G.

Considering that the E parameter is a measure of adsorption force between adsorbent and adsorbate, these results suggest that the interaction between nitrogen and activated carbon decreases with increasing oxygen groups on its surface, which can be associated to the nitrogen quadrupole moment that interacts less than phenol with polar groups on the activated carbon surface.

Another aspect to highlight is the reduction of the C parameter of the BET equation when the oxidation degree of activated carbon increases, in other words, G > GP > GN. This parameter is associated with the residence times of molecules on activated carbon surfaces and it provides an idea of the superficial heterogeneity energetics. This suggests that phosphoric and nitric acid modifications decrease the heterogeneity energetics of activated carbon G.

Figure 2 shows the pore size distribution. It was determined from N_2 isotherms at 77 K using DFT method. The best fitting was obtained using the Quenched Solid Density Functional Theory (QSDFT) for the pore size analysis of geometrically and chemically disordered micro-mesoporous carbons. In this figure, it can be observed that the average pore size for all activated carbons is between 0.3 and 1.4 nm and most pores are about 0.3-0.7 nm. Phosphoric acid impregnation increases the amount of pores in this range while nitric acid impregnation decreases it.

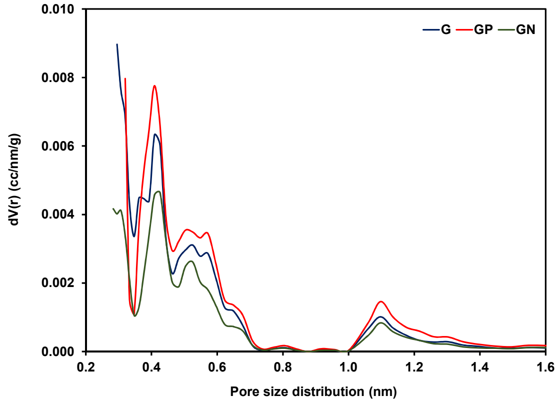

Figure 2. Pore size distribution by DFT (method-slit/cylindr. pores, QSDFT adsorption branch, nitrogen isotherm).

Table 2 shows the results obtained for acidity, basicity and pH at the point of zero charge. As observed, treatment of activated carbon with nitric acid more than doubles the number of acid groups activated on the carbon surface, and impregnation with phosphoric acid also increases these groups, but not to the same proportion. It can also be seen that phosphoric acid impregnation increases the basic group content on the activated carbon surface.

Table 2. Chemical parameters of activated carbons.

Sample	Total acidity (µmol/g)	Total basicity (µmol/g)	Total groups (µmol/g)	pH_{PCZ}
G	641	339	980	8.0
GP	726	521	1247	6.2
GN	1391	360	1751	3.2

Table 3. Sips model parameters.

Parameters	Samples								
	G			GN			GP		
	283 K	291 K	308 K	283 K	291 K	308 K	283 K	291 K	308 K
q_{ms} (mmol/g)	1.769	1.658	1.355	1.858	0.854	1.076	1.901	1.031	1.228
n_s	1.631	1.328	1.208	0.546	2.250	0.096	1.616	0.439	1.048
K_S (L/mmol)	4.943	3.244	10.82	1647	8.116	3.5E+20	4.009	118.1	27.552
r^2	0.986	0.989	0.986	0.984	0.943	0.969	0.995	0.992	0.990

It is noteworthy that impregnations also modify the pH at the point of zero charge from 8.0 for G to 3.2 for GN.

3.2. Phenol solution isotherms

Figure 3 presents the isotherms in aqueous solution, obtained for phenol adsorption on G at three temperatures. They were adjusted to the Sips model in order to obtain the maximum adsorption capacity, process constant and heterogeneity parameter for this model. From Figure 3, it can be seen that phenol adsorption forms a concave isotherm with respect to Ce, and adsorption increases rapidly at concentrations less than 1 mmol/L, where it then begins to slowly grow until it reaches a plateau. This behavior is typical of type I or Langmuir isotherms according to the classification established by Giles [23]. It applies to gas-solid and liquid-solid adsorption and it happens when adsorbed molecules are arranged vertically and there is no strong competition between water and phenol adsorption sites. It may also indicate that there is a strong attraction between the molecules of phenol. Moreover, it can be seen that the adsorption of phenol is favored with decreasing temperature. This fact is attributable to the adsorption of phenol on activated carbon being exothermic and entropy being disadvantaged with decreasing temperature.

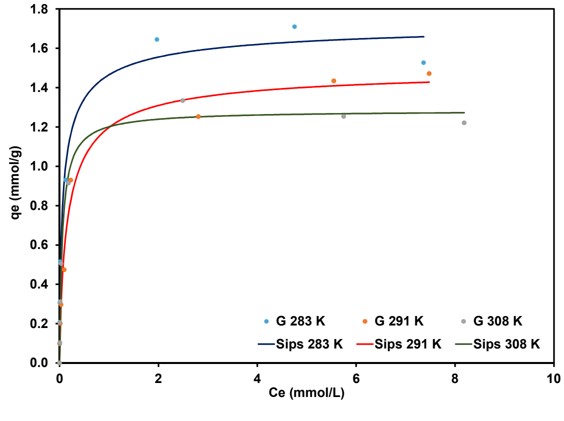

Figure 3. Phenol adsorption from aqueous solution on granular activated carbon G at three temperatures. The lines correspond to an adjustment of points to the Sips model.

Table 3 summarizes the parameters obtained from experimental data adjusted to the Sips model. In Table 3 it can be seen that phenol adsorption on the activated carbon fits to the Sips model with correlation coefficients between 0.984 and 0.995. It can also be observed that adsorption at different temperatures changes the maximum adsorption capacity q_{ms} in the order of 283 > 291 > 308 K for activated carbon, G. Values for the maximum adsorption capacity are between 1.858 and 0.854 mmol/g for activated carbon GN. For activated carbon GP, they are between 1.901 and 1.031 mmol/g. For system heterogeneity given by the n_s parameter, the values obtained are above 1 for most data except for GN to 283 and 308 K and GP to 291 K. As has already been reported [9], values greater than 1 for this parameter are associated with greater heterogeneity in the adsorbent-adsorbate system, therefore, data obtained under 1, suggest a more homogeneous system at these temperatures.

The constant Ks, related to process favorability, increases with temperature for activated carbon GN, while for activated carbons G and GP, different behavior is observed. This could be attributed to the presence of the greatest number of oxygen groups on the surface of activated carbon GN. Regarding to activated carbons G and GP, adsorption processes are also favorable as seen in Figure 4. These results further show the dependence of the parameter Ks with the adsorption temperature and ns parameter decrease with increasing temperature. Figure 4 shows the isotherms obtained for phenol adsorption from aqueous solution for the three activated carbons used. The isotherms correspond to phenol adsorption at 283 K, which as it had been mentioned, is the temperature at which the highest values for adsorption capacity were obtained.

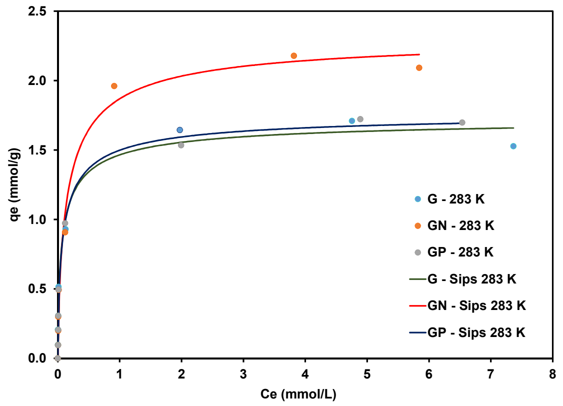

Figure 4. Comparative adsorption of phenol on activated carbons G, GN and GP at 283 K. Lines correspond to the data fitted to the Sips model.

These results show that when comparing the three activated carbons against phenol adsorption, changes made on activated carbon with nitric acid, GN increases adsorption capacity of this, despite the loss of surface area that caused the treatment with the oxidizing agent. In studies of phenol adsorption on activated carbon, it has been found that oxidation of the activated carbon surface decreases the electron density π. Therefore, π-π interactions of the phenolic ring and adsorptivity are decreased [5]. In other studies [24], it has been found that adsorption can also occur by relatively strong specific interactions and they that take place through hydrogen bonds between polar or polarizable molecules and

Table 4. Parameters for the temperature dependent Sips equation.

Sample	**Q (kJ/mol)**	**$K_{S,0}$**	**α**
G	42.5	5.02	3.12
GN	33.3	1335.98	-2.02
GP	-0.5	49.47	17.16

Table 5. Immersion enthalpies of activated carbon in aqueous phenol solutions with standard deviations between 0.21 and 1.10 J/g, and isosteric heat as a function of loading using the Sips equation.

G			**GN**			**GP**		
q_e (mmol/g)	**$-\Delta H_{isost}$ (kJ/mol)**	**$-\Delta H_{inm}$**	**q_e (mmol/g)**	**$-\Delta H_{isost}$ (kJ/mol)**	**$-\Delta H_{inm}$**	**q_e (mmol/g)**	**$-\Delta H_{isost}$ (kJ/mol)**	**$-\Delta H_{inm}$**
0.11	78.0	2152.4	0.11	-13.2	2120.7	0.11	16.5	1610.6
0.21	68.2	1157.8	0.22	7.3	844.6	0.21	10.3	663.5
0.32	61.4	707.0	0.33	21.4	551.9	0.30	6.7	448.3
0.54	52.2	386.2	0.53	46.0	320.4	0.55	-1.5	287.7
0.94	38.9	191.2	0.70	69.9	108.0	0.91	-16.9	115.2
1.43	18.3	87.3	0.83	124.4	203.6	0.98	-24.4	90.6
1.52	10.8	147.0	0.84	127.2	88.9	1.01	-29.8	77.2
1.56	5.5	82.8	0.85	165.9	107.5	1.03	-51.6	71.1

specific sites on the carbon surface that contain oxygenated groups, such as the case of phenol-activated carbon GN system in this study. In other words, nitric acid treatment produces a surface more oxygenated than G.

Regarding the modification with phosphoric acid, it can be seen that the adsorption capacity of activated carbon GP is slightly greater than for G, suggesting that phosphoric acid treatment does not modify significantly the phenol interactions on the activated carbon surface.

3.3. Immersion enthalpies of activated carbon in phenol aqueous solutions

For the activated carbons in this study, immersion enthalpies were determined in phenol solutions at different concentrations, in order to observe changes in enthalpy as a function of phenol concentration and also to evaluate impregnation solid effects with inorganic acids. The heat that occurs when the activated carbon contacts phenol solution is recorded in electric potential graphs versus time. Figure 5 shows the curves obtained for immersing GN in phenol solutions between 20 and 800 mg/L. It is observed that the area under the curve increases with phenol concentration, indicating an increase in the interaction of adsorbate-activated carbon. The immersion enthalpy, ΔH_{im}, is calculated from these plots.

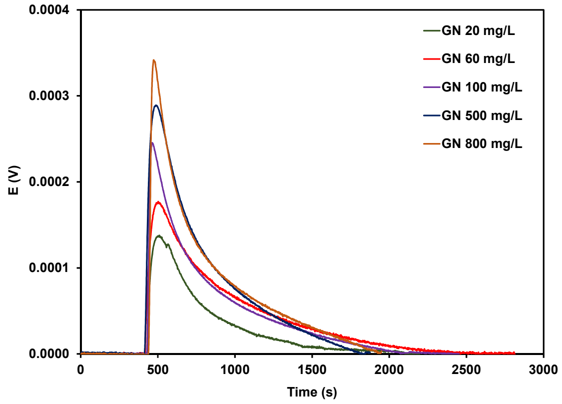

Figure 5. Potentiometric curves for phenol adsorption on activated carbon GN.

3.4. The temperature dependence of the sips equation

As has been observed so far, the quantity of phenol adsorbed on the activated carbon also depends on the temperature. The temperature dependence of the Sips Equation for the affinity constant K_S and the exponent n_S may take the following form [9]:

$$K_S=K_{S,0}.\exp\left[\frac{Q}{RT_0}\left(\frac{T_0}{T}-1\right)\right] \tag{5}$$

$$\frac{1}{n_s}=\frac{1}{n_{S,0}}+\alpha\left(1-\frac{T_0}{T}\right) \tag{6}$$

where $K_{S,0}$ is the adsorption affinity constant at some reference temperature T_0, $n_{S,0}$ is the parameter n at the same reference temperature, R is the constant of the gases, α is a constant parameter and Q is the measure of the adsorption heat.

To obtaine the isosteric heat for the temperature dependence form of the Sips equation, the van't Hoff equation [9] was used:

$$-\Delta H_{iSO}=Q-\alpha RT_0 n^2 \ln\left(\frac{q_e}{q_{mS}-q_e}\right) \tag{7}$$

Table 4 shows the parameters obtained for the temperature dependent Sips equation. The reference temperature used to calculate Q, $K_{S,0}$ and α was T_0 = 283 K.

Table 5 shows the enthalpies obtained for samples of activated carbon in phenol solutions from 0 to 1000 mg/L and the variation of the isosteric heat the amount adsorbed. The isosteric heat in Table 4 was calculated to 291 K.

From Table 5 it can be seen that when comparing the immersion enthalpies of activated carbons in solutions of phenol at 20 to 800 mg/L, in the majority of cases the values decrease in the order of G > GN > GP. These results show that the immersion of activated carbons in phenol solutions of different concentrations is accompanied by a thermal effect resulting from adsorption of both phenol and water. On the other hand, to compare the immersion heat with isosteric heat for the same loading, it is noted that there is a great difference between these. In Figure 6, it can be seen plots of isosteric heat and immersion heat of phenol on each activated carbon versus loading. Figure 6 shows that for the activated carbons G and GP, both the isosteric heat as the heat of immersion decrease with loading while for coal GN the isosteric heat increases with the loading and the heat of immersion decreases with this. In addition, Table 4 shows that the constant α for this sample is negative. This may be the result of increased of oxygen groups produced by treatment with nitric acid. The presence of a greater number of oxygenated groups on the activated carbon surface increases the interaction of these with water molecules, these compete with phenol by active sites on the activated carbon surface and the energy required to desorb water and to adsorb phenol. The phenol adsorption on activated carbon is an exothermic process, the desorption of water from carbon surface is an endothermic process. The results show that when the oxygen groups on activated carbon surface increases, the isosteric heat of Sips equation do not describe the process.

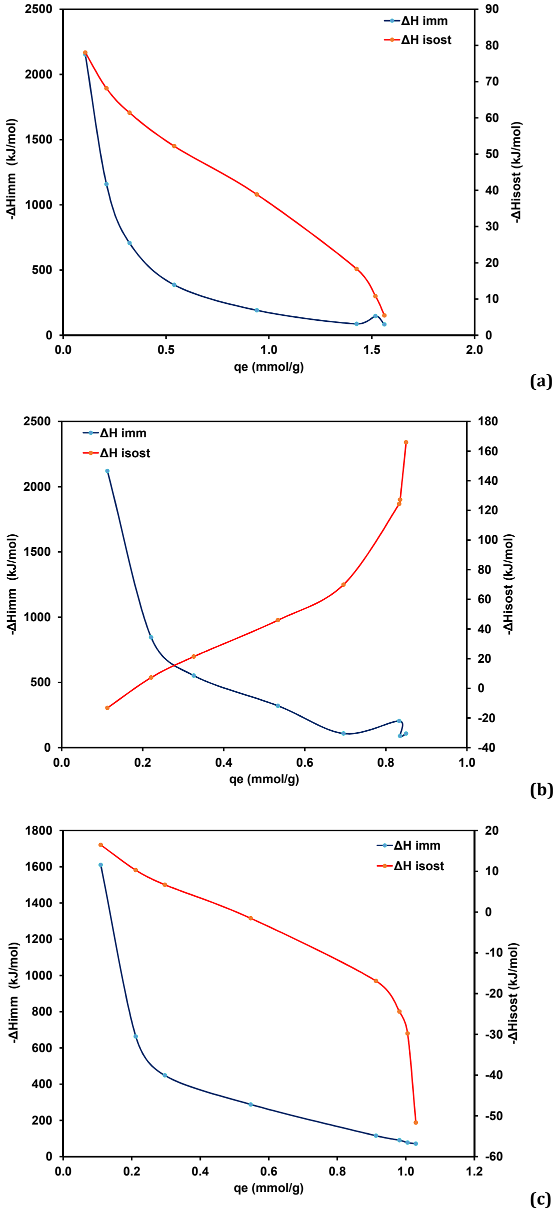

Figure 6. Plots of isosteric heat and immersion heat as a function of loading with phenol. (a) activated carbon G, (b) activated carbon GN and (c) activated carbon GP.

Figure 7 presents the immersion enthalpies as a function of phenol concentration in equilibrium obtained for unmodified activated carbon G in the range of 0 to 800 mg/L, which are adjusted to the Langmuir model. The final phenol concentration, Ce, is calculated using equation (2) of mass balance for a volume of 10 mL that corresponds to the immersion cell used. Figure 7 shows an interesting result since the values of immersion enthalpy as a function of phenol concentration in equilibrium are adjusted, as do the adsorption data to the Sips model when it approaches the Langmuir model. It is noted that the immersion enthalpy values for activated carbon G increase with increasing phenol concentration in equilibrium and as is shown in Figure 7, these variables have a relationship that can be described by the Sips model when considering that $1/n_s$ parameter approaches 1. Knowing that phenol adsorption on activated carbon is an exothermic process and immersion enthalpy increases with amount phenol adsorbed [7-9,25], the Sips equation could be set as follows to describe this process:

$$\Delta H_{inm} = \frac{\Delta H_{imax}.K_{inm}.C_e}{1+K_{inm}.C_e} \qquad (8)$$

where ΔH_{inm} J/g is proportional to the maximum immersion enthalpy, ΔH_{imax} (J/g) and the constant process and K_{inm} which is obtained from the immersion enthalpy at working temperature. The values obtained for these parameters are -ΔH_{imax} 27.29 J/g and K_{inm} 4.62 L/mmol. With respect to modified activated carbons GN and GP, data obtained do not fit to the Sips model, possibly because this was suggested to apply to located adsorption where interactions do not occur [6]. Due to the increased content of oxygenate groups on activated carbon surfaces GN and GP, there are a greater number of interactions between phenol and these activated carbons, which it makes more complex to describe enthalpies in equilibrium.

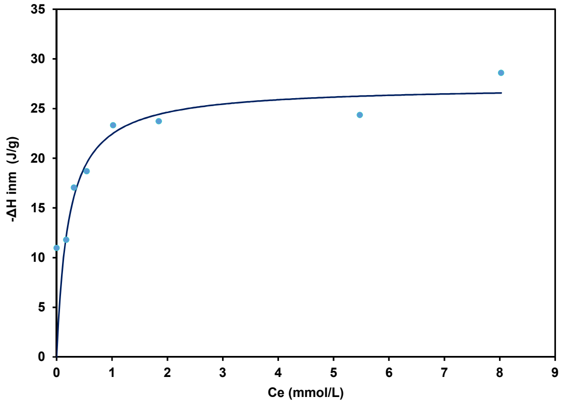

Figure 7. Immersion enthalpy as a function of phenol concentration in equilibrium for activated carbon G. The line corresponds to the data fitted to the Langmuir model.

4. Conclusions

Impregnation of granular activated carbon G with nitric acid solution produces an increase in the phenol adsorption capacity at 308 K. Experimental data of adsorption to activated carbons were adjusted to the Sips model with maximum adsorption capacities between 0.992 and 2.332 mg/g recorded.

Micropore heterogeneity values given by the n term of the Dubinin-Astakhov equation are around 2. Therefore, results obtained for micropore volume by the Dubinin-Astakhov equation are equivalent to those obtained from the Dubinin-Radushkevich equation. Micropore characteristic energies E determined by the Dubinin-Astakhov equation from nitrogen adsorption data at 77 K decrease with impregnation in the order of G > GP > GN.

Pore size distribution determined from nitrogen isotherms at 77 K using DFT allowed us to observe that impregnation with phosphoric acid increases pores in the range of 0.3 to 0.7 nm, while impregnating with nitric acid decreases it.

For phenol adsorption on the activated carbon under study, Langmuir-type isotherms were obtained. They indicate that phenol adsorption is a process performed in monolayer and there is not strong competition between phenol and water for active sites on activated carbon surface. However, values obtained for immersion enthalpies showed that energy is required to desorb water from activated carbons surface and adsorb phenol.

Adsorption is determined at 283, 293 and 303 K and the three temperature isotherms obtained are in accordance with the Sips model. The higher absorption capacities were obtained at 283 K, this is consistent with the fact that phenol adsorption is an exothermic process and is therefore favored when temperature decreases.

Impregnation with nitric and phosphoric acid increases amount of oxygen groups on activated carbon surface and therefore, specific interactions via hydrogen bonds with phenol.

From the immersion enthalpy, it is possible to show that phenol adsorption on activated carbons of the study is an exothermic process and competition between phenol and water for the active sites on activated carbon surface.

For unmodified activated carbon G, a value for ΔH_{imax} of 27.29 J/g was obtained from setting to the Sips model, representing the average value of process at temperature of work, 293 K.

The Sips model can be used to describe the phenol concentration in equilibrium and immersion enthalpy when $1/n_s$ is equal to 1.

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