

Article

Physicochemical Properties of Activated Carbon: Their Effect on the Adsorption of Pharmaceutical Compounds and Adsorbate–Adsorbent Interactions

Valentina Bernal ¹, Liliana Giraldo ¹ and Juan Carlos Moreno-Piraján ^{2,*}

¹ Departamento de Química, Universidad Nacional de Colombia, 11001000 Bogotá, Colombia; vbernal@unal.edu.co (V.B.); lgiraldogu@unal.edu.co (L.G.)

² Departamento de Química, Universidad de los Andes, 11001000 Bogotá, Colombia

* Correspondence: jumoreno@uniandes.edu.co; Tel.: +57-1-3394-949 (ext. 3465, 3478 and 4753)

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Abstract: The adsorption of salicylic acid, acetaminophen, and methylparaben (pharmaceutical products derived from phenol) on carbons activated with different surface chemistries was carried out. We evaluated the effect of the physicochemical properties of the adsorbent and adsorbates on the adsorption capacity. A study of the adsorbate–adsorbent interactions via immersion calorimetry in the analytes solutions at different concentrations was included, in addition to the equilibrium data analysis. The results show that the pharmaceutical compounds (2.28–0.71 mmol g^{−1}) have lower adsorption capacities in the activated carbon with the highest content of oxygenated groups (acids), while the activated carbons with amphoteric characteristics increase the capacities of adsorption (2.60–1.38 mmol g^{−1}). This behavior may be associated with the increased affinity between the adsorbent and solvent due to the presence of polar groups, which was corroborated by the high immersion enthalpy value in water ($\Delta H_{\text{imm}}\text{H}_2\text{O} = -66.6 \text{ J g}^{-1}$). The equilibrium data, adjusted to the Freundlich adsorption model, indicated that the heterogeneous adsorption processes involve immersion enthalpy values between -9.42 and -24.3 J g^{-1} .

Keywords: acetaminophen; activated carbon; adsorption; immersion enthalpy; methylparaben; phenol and salicylic acid; salicylic acid

1. Introduction

The most common use of activated carbons is in adsorption processes, because the adsorbent presents the necessary physicochemical characteristics that allow it to capture substances that are desired to be removed from systems in gaseous or liquid phases [1,2].

Due to anthropogenic activities, water sources are contaminated with substances of different natures: heavy metals, surfactants, products of oil refineries, and chemical agents. Pharmaceutical products, which are considered to be emerging contaminants due to their presence in groundwater, surface water, and drinking water, are included within this last category [3–5].

It is a priority to find effective methods for removing compounds with biological activity, due to their toxicity, from water sources—not only for plants and animals but also for humans who are exposed to it. Active pharmaceutical ingredients such as salicylic acid induce oxidative stress in plants [6]; acetaminophen generates hepatotoxicity and neurotoxicity in aquatic vertebrates [7]; and methylparaben is associated with the proliferation of tumor cells and reproductive abnormalities in humans [8]. Adsorption is a method widely used for the purpose of removing such compounds, due to its low cost of implementation, high efficiency, and easy operational design [9]. Recent research has shown that this process, when carried out in activated carbon, allows the carbon to adsorb at least 50% of the initial concentration of contaminants present in the water [10–12].

The efficiency of the adsorption process depends on the physicochemical characteristics of the adsorbate and adsorbent. For the latter, factors such as the pore size, area, and surface chemistry are relevant if the process is carried out in activated carbon. One of the advantages of this adsorbent is that it allows modifications to the chemical surface through the addition of heteroatoms, such as oxygen, nitrogen, or sulfur, which favor interactions with molecules that are desired to be adsorbed. However, this also increases the affinity with water, because it increases the surface polarity [13,14].

Organic compounds, including pharmaceutical compounds, are apolar. Thus, adsorption can be favored on adsorbents with low surface polarity, so an option to increase the adsorption capacity is to modify the surface chemistry through the reduction of chemical groups present on the activated carbon. This process can be carried out by increasing the adsorbent temperature above the thermal stability of the surface chemical groups on the activated carbon. In this way, the oxygenated groups are converted to CO₂ and CO. According to De la Puente et al. [15], the thermal stability of the main oxygen groups range between 200 K and 1500 K. Table 1 shows the temperature range of the thermal stability of the main oxygenate groups present on activated carbon.

Table 1. Thermal stability temperature of functional groups on activated carbon.

Functional Group	Thermal Stability Temperature (K)
Carboxylic acid	523–673
Lactone	673–923
Phenol	623–923
Carbonyl	973–1173
Quinone	1073–1173
Pyrone	1273–1473

Sigmund et al. indicated that aromatic compounds such as phenols increase their adsorption capacity if π - π interactions between the adsorbate and adsorbent occur [16]. Activated carbon, due to its aromatic nature, possesses this type of electron. However, according to Long et al., if the adsorbents are subjected to high temperatures, they increase the amount of these electrons, which causes the sites to become highly basic. Therefore, adsorbates with acidic characteristics can be selectively adsorbed [17].

In this work, the adsorption of phenol, salicylic acid, acetaminophen, and methylparaben on five activated carbons with different surface chemistries—a granular activated carbon made from coconut shell (CAG) subjected to an HNO₃ oxidation or heat treatment at different temperatures (1073 K, 1173 K, and 1273 K)—was carried out. The effect of the physicochemical changes of the adsorbent in the adsorption capacity of the compounds was determined from the equilibrium data (adsorption isotherms), and the adsorbate-adsorbent affinity was evaluated by immersion enthalpy in the studied compound solutions.

2. Materials and Methods

2.1. Activated Carbons

Table 2 discloses preparation methods of the activated carbons analyzed in this work.

Table 2. Modifications made to carbon activated granular (CAG).

Activated Carbon	Modification Method
CAG	Granular activated carbon (CAG) (CARBOCHEM CARBOCHEM GS50 INC., Philadelphia, PA, USA) immersed in concentrated HCl, rinsed with distilled water until reaching a constant pH value, and dried at 373 K.
CAO	Oxidized activated carbon (CAO). Activated carbon CAG immersed in HNO ₃ (6 M) for 6 hours until it reached its boiling temperature, washed with distilled water until reaching a constant pH value, and dried at 373 K.
CAR1073, CAR1173, and CAR1273	Reduced activate (CAR). Activated carbon subjected to heat treatment in a THERMOLYNE oven for 2 hours with a heating ramp of 2 K min ⁻¹ at 1073, 1173, or 1273 K, respectively.

2.2. Physical Characterization

Nitrogen adsorption at 77 K was performed in a commercial semi-automatic Autosorb IQ2 (Quantachrome Instruments, Boynton Beach, FL, USA) after degassing the activated carbons for 24 h at 473 K. The Brunauer, Emmett, and Teller (BET); Dubinin–Astakhov; and density functional theory (DFT) models were applied to the isotherms to obtain models for the determination of the apparent surface area, micropore volume, and distribution of pore sizes, respectively.

2.3. Chemical Characterization

2.3.1. The Determination of Surface Chemistry (Oxygenated Functional Groups) of the Activated Carbon

Boehm's method allows the determination of the oxygenated chemical groups (phenols, lactones, and carboxylic acids). It corresponds to the acid–base titration of the functional groups present on the activated carbon surface with bases that have different strengths, which allows the neutralization of acids with different pKa values [18].

This method was carried out on an Ohaus Pioneer PA 114 analytical balance (Ohaus Corporation, Parsippany, NJ, USA), with an accuracy of 0.001 g. First, 0.5 g of activated carbon CAG was weighed out in airtight glass containers. Next, 0.05 L of a NaOH solution 0.1 M was added, and maintained at room temperature (293 ± 1 K) for 5 days with constant agitation at 100 rpm. Subsequently, an aliquot of the supernatant was taken and titrated with HCl using a potentiometer CG840 Schott (Schott AG, Maguncia, Germany). The above procedure was repeated using sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3) as the immersion liquids.

For the quantification of basic groups, the previous procedure was carried out using 0.05 L of HCl 0.1 M as the immersion liquid. This was maintained for 5 days, an aliquot of supernatant was taken and it was titrated with 0.1 M NaOH.

The solutions of HCl and NaOH were previously standardized with boric acid and potassium biftalate.

2.3.2. pH Determination of the Zero Charge Point

Some properties associated with the adsorption on solid–liquid systems are influenced by the appearance of surface electric charges in the adsorbent and the adsorbate.

When activated carbon is placed in contact with an electrolytic solution, the surface ionizes depending on the pKa of the functional groups present in the surface, and the charged particle is surrounded by ions of the opposite charge since it is apparently electrically neutral. The pH value required for the net surface charge of activated carbon is zero and is known as the point of zero charge (pHpzc).

The mass titration method was proposed by Noah and Schwartz for the determination of the net charge of alumina oxides in solution. This technique consists in measuring a pH value that becomes constant with the increase in mass of the solid in a volume of water. Under these conditions, it has been observed that the pH of the oxide aqueous suspension depends on the amount of this material in a given volume of water [19].

On an Ohaus Pioneer PA 114 balance (Ohaus Corporation, Parsippany, NJ, USA), with an accuracy of 0.001 g, between 4 g and 4.5 g of activated carbon was weighed in amber glass containers with lid, to which was added 0.01 L of a solution of NaCl 0.1 M. The containers are stored for 5 days at ambient temperature (293 ± 1 K) and constant agitation (100 rpm); past the equilibrium time, 0.005 L of the supernatant solution of each container was extracted and the pH was measured with a pH meter CG 840 Schott (Schott AG, Maguncia, Germany).

2.4. Adsorption Test

2.4.1. Preparation of Pharmaceutical Compound Solutions

Adsorption tests were carried out using solutions of phenol, salicylic acid, acetaminophen, and methylparaben in concentrations between 0.07 and 10.6 mmol L⁻¹, since at these concentrations there is a sufficient amount of adsorbate molecules to evaluate the adsorbate-adsorbent interactions without the interference of the activated carbon-solvent interactions. Stock solutions were prepared with analytical grade reagents: phenol (Merck Millipore, MA, USA) with a purity of 99%, salicylic acid (Panreac chemistry SLU, Castellar del Vallès, Barcelona, Spain) with a purity of 99%, acetaminophen (Alpha Aesar, MA, USA) with a purity of 98%, and methylparaben (Panreac chemistry SLU, Castellar del Vallès, Barcelona, Spain) with a purity of 99%. The solutions were prepared by dissolving 2 g of the reagent in 1 L of distilled water, stirring at 150 rpm and 293 ± 1 K. The dilutions were made by taking stock solution aliquots and adjusting the volume with distilled water.

2.4.2. Batch Experiments

First, 0.1 g of activated carbon CAG was weighed in amber glass containers, to which 0.025 L of the analyte solution (phenol, salicylic acid, acetaminophen, and methylparaben) was added with concentrations between 0.07 mmol L⁻¹ and 10.6 mmol L⁻¹. The containers were kept at room temperature (293 ± 1 K) and with sporadic agitation for 7 days (150 rpm). Once the equilibrium time was reached, the solutions were filtered and the equilibrium concentration was determined by UV-Vis spectrophotometry (Thermo Fisher Scientific, Madison, WI, USA) at the maximum wavelength of the analyte. Table 3 shows the maximum wavelengths used for each analyte.

Table 3. Maximum wavelengths of the analytes.

Compound	λ_{\max} H ₂ O (nm)
Phenol	268
Salicylic acid	296
Acetaminophen	242
Methylparaben	254

The concentration equilibrium was calculated from the calibration curve. Equation (1) is used to determine the adsorbed amount of analyte:

$$Q = \frac{(C_o - C_e) * V}{m}, \quad (1)$$

where Q represents the adsorbed amount, C_o the initial concentration, C_e the equilibrium concentration, V the total volume of solution, and m the mass of activated carbon employed.

2.5. Calorimetric Assays

The immersion enthalpy on the activated carbons CAG, CAO, CAR1073, CAR 1173, and 1273 CAR were determined in aqueous solutions of phenol, salicylic acid, acetaminophen, and methylparaben with concentrations between 0.07 and 10.6 mmol L⁻¹. For this purpose, a Tian-Calvet calorimeter of local construction was employed, in which 0.01 L cell of immersion liquid was deposited. Activated carbon (0.1 g) was previously weighed out in a glass ampoule with a fragile peak in the bulb that facilitates its later break at the immersion time. The glass ampoule was placed on the top of the calorimeter. The electric potential was recorded until reaching a baseline, and then the immersion of the activated carbon was carried out. The increase in potential is associated with the immersion, and once the value returned to the baseline, and electrical calibration was performed.

The immersion enthalpy is obtained using Equations (2) and (3):

$$Q_{imm} = K_{cal} * \text{area under the immersion curve} \quad (2)$$

$$\Delta H_{imm} = \frac{-Q_{imm}}{m} \quad (3)$$

where Q_{imm} represents the heat of immersion, K_{cal} is the calibration constant of the calorimeter determined from the electrical calibration, and the area under the curve is the integral of the potential's peak generated during the adsorption.

3. Results and Discussion

3.1. Physicochemical Characterization of Activated Carbons

3.1.1. Textural Characterization

Table 4 shows the values of surface area and pore size of the activated carbons CAG, CAO, CAR1073, CAR 1173, and CAR 1273, determined by BET and Dubinin–Astakhov models, respectively.

Table 4. Textural characteristics of activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

Textural Characteristic	CAO	CAG	CAR1073	CAR1173	CAR1273
Surface area (S_{BET}) ($\text{m}^2 \text{g}^{-1}$)	469	864	1127	814	711
Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	0.18	0.34	0.42	0.29	0.23
Total volume ¹ ($\text{cm}^3 \text{g}^{-1}$)	0.21	0.35	0.48	0.34	0.30

¹ Calculated with the DFT (quenched solid density functional theory) method, assuming slit cylindrical pores.

According to the data in the Table 4, it is evident that the oxidation treatment with nitric acid decreases the surface area, micropore volume, and total volume of pores compared to the results of the activated carbon CAG. Gokce et al. [20] indicated that this behavior is due to the conversion of micropores into mesoporous by the effect of strong oxidation. Moreover, the decrease in the surface area is associated with the pores blocking due to the formation of acid groups that prevent nitrogen access through the activated carbon structure. According to Shim et al. [21], the formation of acid groups tends to occur to in the edges pores because it is the weakest part of the carbonaceous structure. Furthermore, the graphenic layers are very stable, so the oxidation there is very slow.

With respect to the activated carbon CAG, it was determined that the increase in the thermal treatment temperature above 1073 K decreases its textural characteristics, while up to 1073 K the parameters increase. For activated carbons CAR1173 and CAR1273, it was determined that the decrease in the textural properties is associated with pore blockage with gases (CO , CO_2) originating during the thermal treatment [22]. In addition, this behavior can be caused by the collapse of carbonaceous structures due to temperature; this is observed in the decrease of the total volume and micropore volume values (see Table 4). Hu et al. indicated that low temperatures of burn-off favored the formation of microporosity, as is the case of activated carbon CAR1073. Likewise, the increase of this type of pores favors the adsorption of nitrogen, which generates an increase in the textural parameters for this sample [23].

Figure 1 shows the pore size distribution of the activated carbons. It can be observed that these samples have pores between 10 and 14 Å—pores suitable for the adsorption of molecules such as phenols, which have areas smaller than this value.

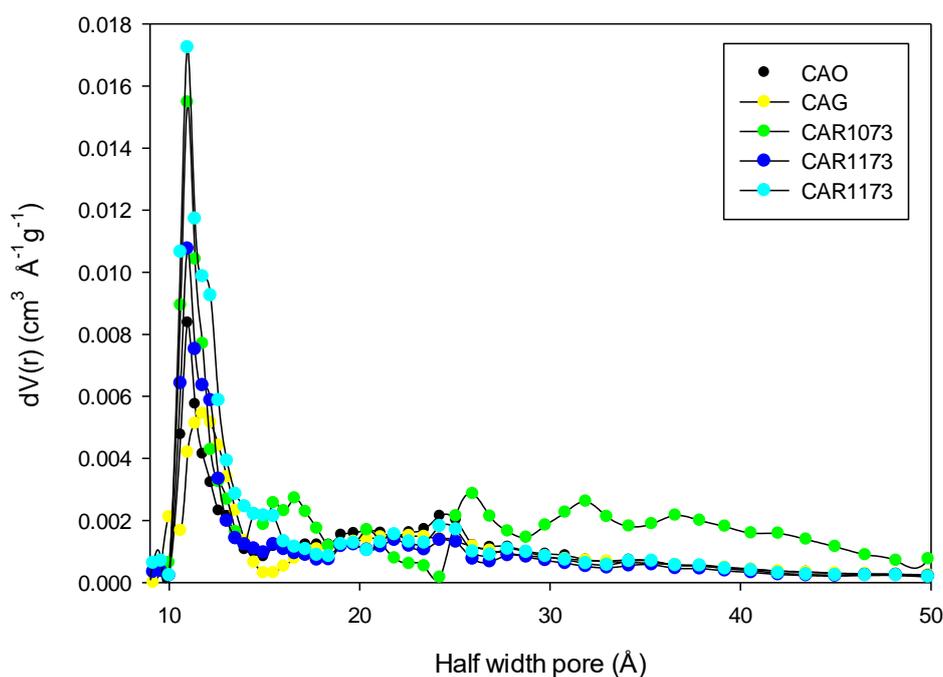


Figure 1. Pore size distributions of the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

3.1.2. Chemical Characterization

Table 5 shows the results of the chemical characterization of activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

Table 5. Chemical characteristics of the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

Chemical Characteristic	CAO	CAG	CAR1073	CAR1173	CAR1273
Total acidity ($\mu\text{mol g}^{-1}$)	656	90.5	93.6	93.0	94.1
Total basicity ($\mu\text{mol g}^{-1}$)	735	742	1210	2037	2290
Carboxylic acid ($\mu\text{mol g}^{-1}$)	106	22.2	66.1	65.5	64.7
Lactones ($\mu\text{mol g}^{-1}$)	490	21.8	21.2	23.8	46.8
Phenols ($\mu\text{mol g}^{-1}$)	53.9	46.6	6.36	3.71	17.5
pH_{pzc}	3.40	5.40	11.1	8.90	9.96

Table 5 presents the results of the chemical characterization of the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273. It can be observed that activated carbon CAO has the highest amount of acid groups (lactones > carboxylic acid > phenols) due to the oxidation with nitric acid, which gives it a total acidity higher than the rest of the studied activated carbons. Boehm indicated that strong oxidations generate functional groups such as carboxylic acids and phenols [18], and that groups such as the lactones are the product of the condensation of phenols and vicinal carboxylic acid groups during thermal treatment. In activated carbon CAG, it is evident that phenol groups are prevalent because coconut shell is constituted by lignin, cellulose, and hemicellulose, which are polymers with abundant phenol contents.

The CAR1073, CAR1173, and CAR1273 activated carbons have a total acidity equivalent to that of the starting activated carbon. However, at the temperature of thermal treatment their reduction was expected, therefore the formation of acid groups after the thermal treatment was attributed to the reaction between free radicals generated by the breakdown of the carbonaceous chains in the heat treatment and environmental oxygen-forming groups such as carboxylic acids [24].

The formation of acid groups results in greater surface polarity. Therefore, contacting activated carbons with water will generate an interaction with this solvent, depending on the affinity that is established between them. To establish this relation for the studied activated carbons, water immersion calorimetry was performed, and the results are shown in Table 6.

Table 6. Immersion enthalpy in water for activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

$\Delta H_{\text{imm}}^{\text{CAO}}$ (J g^{-1})	$\Delta H_{\text{imm}}^{\text{CAG}}$ (J g^{-1})	$\Delta H_{\text{imm}}^{\text{CAR1073}}$ (J g^{-1})	$\Delta H_{\text{imm}}^{\text{CAR1173}}$ (J g^{-1})	$\Delta H_{\text{imm}}^{\text{CAR1273}}$ (J g^{-1})
-66.6 ± 1.33	-49.7 ± 0.99	-27.3 ± 0.55	-32.4 ± 0.65	-31.5 ± 0.63

According to the results of Table 6, the activated carbon with greater immersion enthalpy values in water was the activated carbon modified with nitric acid, CAO; therefore, the greater the number of acid groups, the higher the affinity with the solvent due the greater surface polarity.

In the case of activated carbon CAG, the immersion enthalpy in water was greater than the activated carbons with heat treatment. When associating the data of the chemical characterization with these results, it was found that this activated carbon had a greater amount of phenol groups, so it was determined that the adsorbent-solvent interaction was associated with the formation of hydrogen bonds interactions between phenol and water. Figure 2 shows that for the studied activated carbons, there was a directly proportional relationship between the amount of surface phenols and the enthalpy of immersion in water.

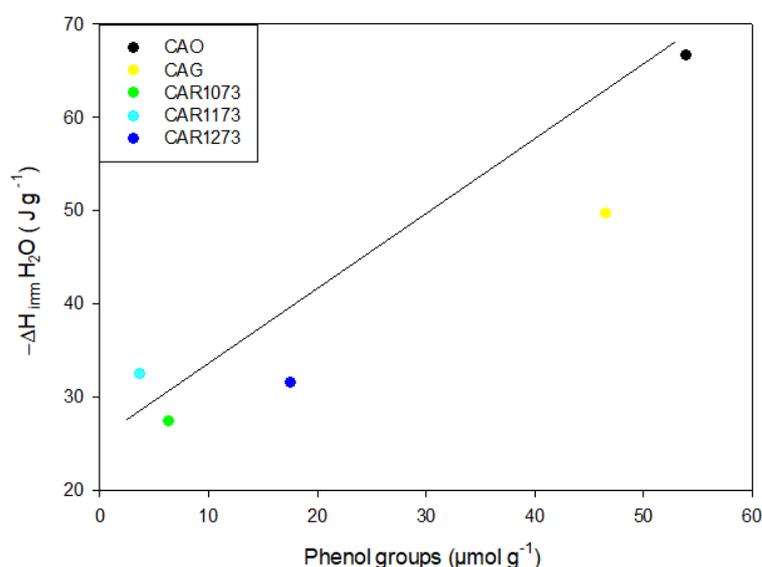


Figure 2. Relationship between the amount of phenol groups and the enthalpy of immersion in water of the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

The basicity in the activated carbons was attributed to the formation of oxygenated functional groups, such as pyrone, chromene, diketone, and quinone, as well as the delocalized electrons π of the graphenic layers. Montés-Morán et al. [25] indicated that the basicity of groups like pyrones is low; however, if the group is included in cycles of more than one ring, the pKa increases above 12 due to a stabilization of the protonated form through the conjugation of π electrons with sp^2 structures.

On the other hand, the basicity of the π electrons was evaluated from the adsorption of H^+ ions in the graphene layers, a process that was carried out by electrostatic interactions. According to Montés-Morán, delocalized π electrons are the main contributors to the basicity of activated carbon, as they are found in a greater proportion compared to the number of basic functional groups.

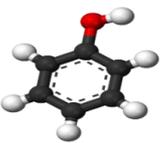
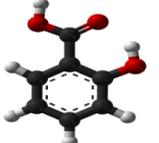
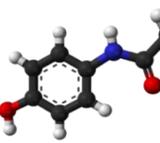
The pH of the point of zero charge is one of the physicochemical parameters with greater relevance in the adsorption processes carried out in aqueous solutions, because it indicates the net charge from the adsorbent when it comes in contact with water. The pH of the point of zero charge is dependent on the surface chemistry of the adsorbents. As such, activated carbons with a high content of acid groups present a pH of the point zero charge below 7 (such as CAO), while activated carbons with basic structures present values above this pH (CAR). In terms of electric charge, Noah et al. [19] indicated that at the pH of the point of zero charge the surface of the activated carbon is neutral, while below this value the surfaces have a positive charge due to the protonation of functional groups such as amines. At pH values above this given value, the electric charge of the adsorbent is negative due to the deprotonation of functional groups such as phenols and carboxylic acids. Thus, at the pH of the solutions (around 6), the activated carbon carbon CAO had a negative surface charge while the other activated carbons had a positive charge.

It can be observed from the values shown in Table 5 that the pH of the point of zero charge increases in proportion to the basic groups present on the activated carbons of study. In addition, a decrease in the pH of the point of zero charge of the activated carbons CAR1173 and CAR1273 was shown; this behavior was attributed to the increase of the basicity by π electrons and not by functional groups that can donate or accept protons with the medium; therefore, part of the basicity cannot be quantified through the pH.

3.2. Adsorption Test

The adsorption processes not only depend on the physicochemical characteristics of the adsorbents; properties such as solubility, molecular size, molecular weight, and pKa are also relevant to the processes carried out in solution. Table 7 shows the physicochemical characteristics of phenol, salicylic acid, acetaminophen, and methylparaben.

Table 7. Physicochemical characteristics of phenol, salicylic acid, acetaminophen, and methylparaben.

Physicochemical Characteristic	Phenol	Salicylic Acid	Acetaminophen	Methylparaben
Structure				
Molecular size (\AA^2)	5.76×4.17	6.96×5.87	8.50×5.70	8.69×5.02
Solubility H_2O 298 K (mol L^{-1})	0.882	0.017	0.093	0.016
pKa	9.99	2.97	9.34	8.20

Red spheres represent the oxygen atoms, blue spheres the nitrogen atoms, black spheres the carbon atoms, and white spheres the hydrogen atoms.

It is shown in Table 7 that the adsorbates present differences in their physicochemical characteristics despite having in common the group structure phenol. Properties such as solubility and pKa vary depending on the substituent present in the aromatic ring; for example, the presence of groups such as carboxylic acid (salicylic acid) and ester (methylparaben) decrease the solubility of the compounds, which is an indication that the adsorbate–solvent interactions are disfavored, a step that is required for the adsorption to take place. Except for salicylic acid, the other compounds have values of pKa above pH 8, which indicates that above this pH, 50% of the initial concentration of the adsorbate is ionized.

Adsorption Isotherms

The data of the adsorption equilibrium allows the determination of the amount of compound that can be adsorbed in each activated carbon once the equilibrium time has been reached. In general, once the adsorption isotherms are determined, it is possible to adjust the data to a mathematical model that describes the experimental behavior from chemical, kinetic, or thermodynamic assumptions. Figures 3–7 show the adsorption isotherms of phenol, salicylic acid, acetaminophen, and methylparaben in the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

The isotherms were fitted to the Langmuir, Freundlich, Redlich-Peterson, and Sips models, and the parameters of each model can be found in Tables 7–12.

The selection of the adsorption models used allows the description of different types of systems. The Langmuir model is used for adsorption processes where the adsorbate-adsorbent interactions are specific, and all active sites are energetically equivalent; therefore, the process are considered homogeneous.

The Freundlich, Sips, and Redlich-Peterson models describe systems that present high energetic heterogeneity associated with the formation of nonspecific interactions that include lateral and associative interactions. In the Freundlich model, it is assumed that the adsorbate interacts with different active sites that differ in the energy they possess; therefore, the energy of the process is not constant.

The Sips and Redlich-Peterson models are derived from the Freundlich and Langmuir models, allowing the description of systems that exhibit intermediate behavior [26–28].

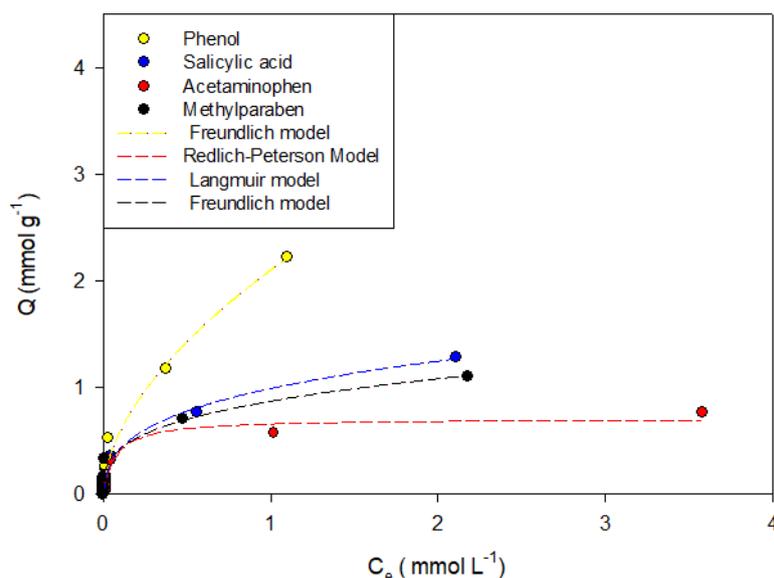


Figure 3. Adsorption isotherm of phenol, acetaminophen, salicylic acid, and methylparaben on activated carbon CAO at 293 K.

Table 8. Parameters of Langmuir, Freundlich, Redlich-Peterson, and Sips models for phenol, acetaminophen, salicylic acid, and methylparaben adsorption on activated carbon CAO.

Compound	Model	K_1^a	K_2 ($L^{-1} \text{ mmol}$)	Q_m (mmol g^{-1})	n	R^2
Phenol	Freundlich	2.10	NA ^b	NA	0.56	0.98
Salicylic acid	Redlich-Peterson	24.5	23.8	NA	0.69	0.99
Acetaminophen	Langmuir	9.14	NA	0.71	NA	0.96
Methylparaben	Freundlich	0.87	NA	NA	0.31	0.97

^a Corresponds to the equilibrium constant and its units depend on the model of adjustment K_L (Langmuir constant) and $KR-P$ (Redlich-Peterson constant) = $L \text{ g}^{-1}$, K_F (Freundlich constant) = $(\text{mmol}^{1-1/n} L^{1/n} \text{ g}^{-1})$ and K_S (Sips constant) = $(L \text{ mmol}^{-1})$. ^b NA: Not applicable.

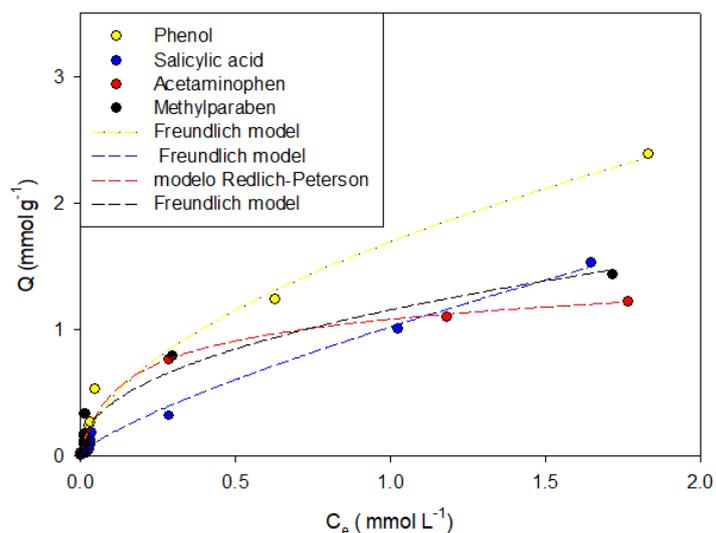


Figure 4. Adsorption isotherm of phenol, acetaminophen, salicylic acid, and methylparaben on activated carbon CAG at 293 K.

Table 9. Parameters of Freundlich and Redlich-Peterson models for phenol, acetaminophen, salicylic acid, and methylparaben adsorption on activated carbon CAG.

Compound	Model	K_1	K_2 ($L^{-1} \text{ mmol}$)	Q_m (mmol g^{-1})	n	R^2
Phenol	Freundlich	2.25	NA	NA	0.58	0.98
Salicylic acid	Freundlich	1.34	NA	NA	0.77	0.99
Acetaminophen	Redlich-Peterson	11.1	9.56	NA	0.86	0.98
Methylparaben	Freundlich	1.57	NA	NA	0.45	0.97

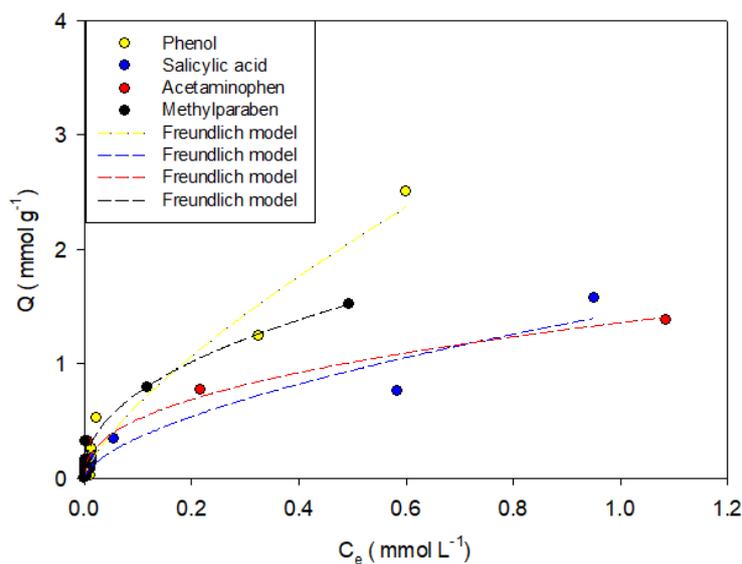


Figure 5. Adsorption isotherm of phenol, acetaminophen, salicylic acid, and methylparaben on activated carbon CAR1073 at 293 K.

Table 10. Parameters of Freundlich model for phenol, acetaminophen, salicylic acid, and methylparaben adsorption on activated carbon CAR1073.

Compound	Model	K_1	K_2 ($L^{-1} \text{ mmol}$)	n	R^2
Phenol	Freundlich	3.44	NA	0.73	0.96
Salicylic acid	Freundlich	1.44	NA	0.61	0.94
Acetaminophen	Freundlich	1.36	NA	0.42	0.97
Methylparaben	Freundlich	2.08	NA	0.45	0.98

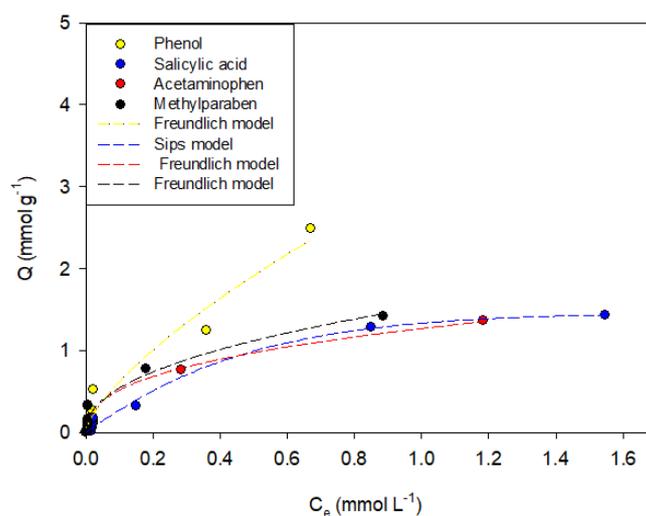


Figure 6. Adsorption isotherm of phenol, acetaminophen, salicylic acid, and methylparaben on activated carbon CAR1173 at 293 K.

Table 11. Parameters of Freundlich and Sips models for phenol, acetaminophen, salicylic acid, and methylparaben adsorption on activated carbon CAR1173.

Compound	Model	K_1	Q_m (mmol g^{-1})	n	R^2
Phenol	Freundlich	3.11	NA	0.70	0.96
Salicylic acid	Sips	4	1.35	11.4	0.99
Acetaminophen	Freundlich	1.27	NA	0.43	0.97
Methylparaben	Freundlich	1.53	NA	0.45	0.96

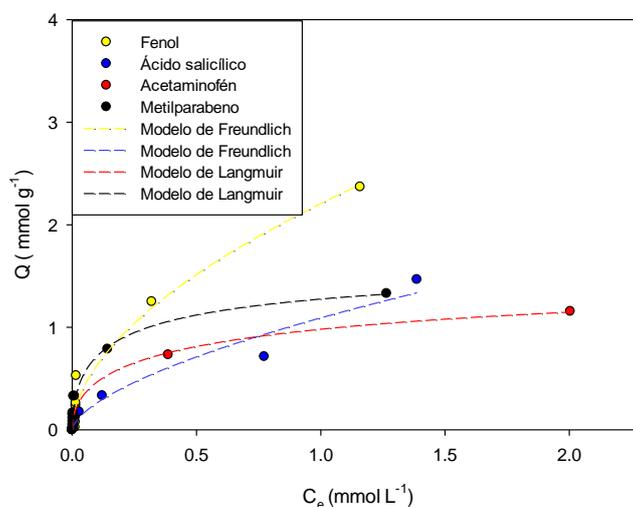


Figure 7. Adsorption isotherm of phenol, acetaminophen, salicylic acid, and methylparaben on activated carbon CAR1273 at 293 K.

Table 12. Parameters of Langmuir and Freundlich models for phenol, acetaminophen, salicylic acid, and methylparaben adsorption on activated carbon CAR1273.

Compound	Model	K_1	K_2 (L^{-1} mmol)	Q_m ($mmol\ g^{-1}$)	n	R^2
Phenol	Freundlich	2.21	NA	NA	0.54	0.97
Salicylic acid	Freundlich	1.09	NA	NA	0.62	0.96
Acetaminophen	Langmuir	25.3	NA	1.02	NA	0.93
Methylparaben	Langmuir	44.2	NA	1.20	NA	0.94

The models of Freundlich and Redlich–Peterson do not include in their parameters the adsorption capacity; however, by replacing in the mathematical equations the calculated parameters of each model and taking C_e as the higher equilibrium concentration, it is possible to calculate a theoretical capacity of adsorption. The results are shown in Table 13.

Table 13. Adsorption capacities calculated with Freundlich, Langmuir, Redlich–Peterson, and Sips models for the adsorption of phenol, acetaminophen, salicylic acid, and methylparaben on the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

Adsorbate	Activated Carbon	Model	Q ($Mmol\ g^{-1}$)
Phenol	CAO	Freundlich	2.28
	CAG	Freundlich	2.58
	CAR1073	Freundlich	2.60
	CAR1173	Freundlich	2.50
	CAR1273	Freundlich	2.40
Salicylic acid	CAO	Redlich–Peterson	1.30
	CAG	Freundlich	1.37
	CAR1073	Freundlich	1.51
	CAR1173	Sips	1.35
	CAR1273	Freundlich	1.42
Acetaminophen	CAO	Langmuir	0.71
	CAG	Redlich–Peterson	1.21
	CAR1073	Freundlich	1.38
	CAR1173	Freundlich	1.36
	CAR1273	Langmuir	1.02

Table 13. *Cont.*

Adsorbate	Activated Carbon	Model	Q ($Mmol\ g^{-1}$)
Methylparaben	CAO	Freundlich	2.20
	CAG	Freundlich	1.43
	CAR1073	Freundlich	1.53
	CAR1173	Freundlich	1.44
	CAR1273	Langmuir	1.20

It can be observed that the adsorption isotherms presented in Figures 3–7 are mainly fitted to the adsorption models that contemplate within their parameters the energetic heterogeneity derived from the physicochemical characteristics of the system. The Freundlich model fits the adsorption data of most systems; this indicates that the process is carried out by the formation of multilayers with heterogeneous distributions of the adsorption enthalpy. According to the model, the energy decreases exponentially and remains constant once the process has reached equilibrium [29]. From the point of view of statistical thermodynamics, the value of the heterogeneity factor (n) depends on the coordination number of the adsorbate, adsorbate–adsorbate interactions, the Boltzmann constant, and Avogadro’s number; therefore, the heterogeneity of the systems depends on the binding energy of the active sites and the formation of lateral interactions. Values of n that tend to 0 indicate

physisorption, while values close to 1 indicate chemisorption or cooperative adsorption [30]. In the case of Redlich-Peterson and Sips models, when n tends to 0 the equation takes the form of the Freundlich model and when it tends to 1 the Langmuir model is adopted.

Additionally, the energetic heterogeneity of the systems is attributed to the competition between the solvent and the adsorbate for the active sites, which means that the enthalpy of adsorption is not constant throughout the process. Likewise, the change in the adjustment models shows that the adsorption depends on the type of adsorbate–adsorbent interactions, which not only depends on the chemical groups present in the adsorbent.

It was found that phenol adsorption can be described in all systems with the Freundlich models, indicating that the process is highly heterogeneous, which in turn is indicative of the formation of adsorbent-adsorbate, adsorbate–solvent interactions and interactions between molecules that are already adsorbed, which in this case may be hydrogen bonds. This same trend describes the behaviors of salicylic acid, methylparaben, and acetaminophen. However, the adsorption of the latter compound on the activated carbons CAO and CAR1273 are described with the Langmuir models, indicating specific adsorbate–adsorbent interactions, so that the adsorption capacity decreases.

To determine the effect of the textural characteristics on the adsorption capacity, the adsorption capacity was associated with the micropore volume. Figure 8 shows the results obtained.

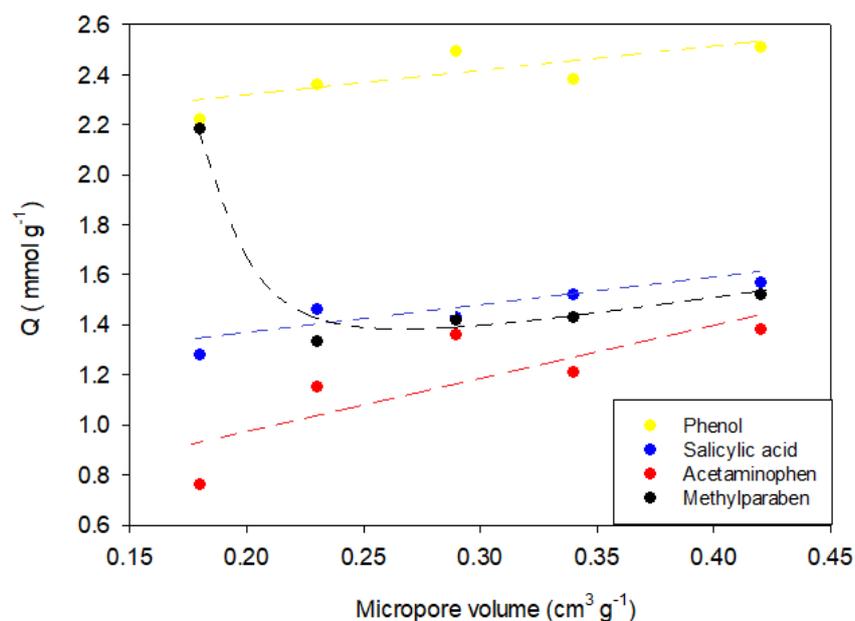


Figure 8. Relation between the adsorption capacity of phenol, acetaminophen, salicylic acid, and methylparaben and the micropore volume of activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273. Dashed lines represent a tendency of data.

Figure 8 shows a directly proportional behavior between the adsorption capacity and the micropore volume. This indicates that the process of adsorption of the study compounds is related to the filling of micropores according to the energy they possess. In the case of acetaminophen and phenol, adsorption on CAR1173 was not found to present this tendency, since the capacity of adsorption in this case was greater than that of activated carbon CAG, even though the latter has a greater surface area and micropore volume (Table 4). A similar behavior was presented by methylparaben, whose adsorption capacity was greater in the activated carbon CAO, which presented the lowest values of surface area and micropore volume. These deviations from the general behavior were attributed to the effect of surface chemistry on the adsorption capacity.

According to the data in Table 4, the activated carbons studied are microporous, which could limit the process of adsorption of large molecules, although this is not the case of phenol, salicylic

acid, acetaminophen and methylparaben, which have small dimensions. The presence of the aromatic substituents could generate steric hindrance, so the effect of the substituent on the adsorption capacity of the adsorbates on activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273 was evaluated.

In Figure 9, it is evident that the behavior between the adsorption capacity and the weight of the substituent is inversely proportional in all activated carbons, as indicated by Lundelius' rule. For the correlations presented, the slope represents the rate of change in the adsorption capacity for each gram of additional substituent from the phenolic ring. The intercept corresponds to the contribution of the phenolic ring to the adsorption capacity. It is evident that the effect of the weight of the substituent in the adsorption capacity (slope) does not vary between the activated carbons CAG, CAR1073, CAR1173, and CAR1273; therefore, a linear function can be employed to describe the general behavior in the four activated carbons. CAO presents a slope different from that of the other activated carbons; as such, its behavior was described with a different equation.

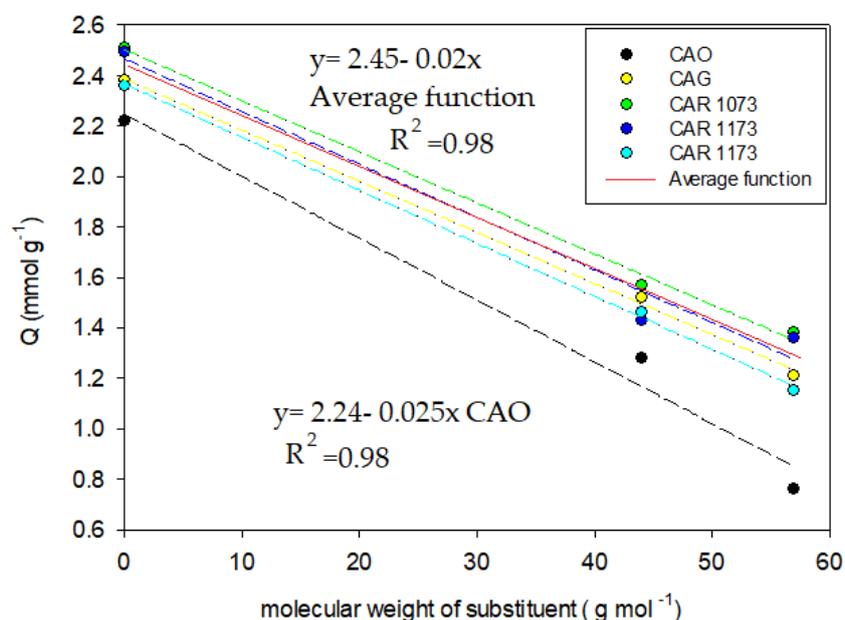


Figure 9. Relation between the molecular weight of the substituent and the adsorption capacity of the adsorbates on the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

In Figure 9 it can be seen that the adsorption capacity (Q) decreases with the molecular weight of the substituent (Q phenol $>$ Q salicylic acid = carboxylic acid $>$ Q acetaminophen = amide \geq Q methylparaben = ester). Also, according to the slope of the equations, the adsorption capacity varies by 0.02 mmol g^{-1} for each gram from the substituent in the phenolic ring. In the activated carbon CAO, the adsorption capacity decreased by 25% with the increase in the molecular weight of the substituent ($b = 0.025 \text{ mmol g}^{-1}$). This may be related to the decrease in the volume of micropores, but also to the presence of oxygenated groups in the entries of this type of porosity, which generates steric hindrance with the substituents in the adsorbates.

The process of adsorption of organic compounds from aqueous solutions can involve two driving forces: a derivative of the hydrophobicity of the solute that induces adsorption by low adsorbate-solvent affinity and the specific affinity of the adsorbate for the surface, which contemplates the adsorption by ionic interactions, by van der Waals forces, and by chemical reactions. Therefore, the adsorbate-adsorbent affinity depends on the surface chemistry of the activated carbon.

To analyze the correlation between the adsorbed amount and the functional groups present in the activated carbons, it was determined that the adsorbed amount of phenol, salicylic acid, and acetaminophen increases in a manner that is inversely proportional to the total acidity of the activated

carbons. Figure 10 shows the relationship between the total basicity and the adsorbed amount of phenol, salicylic acid, and acetaminophen.

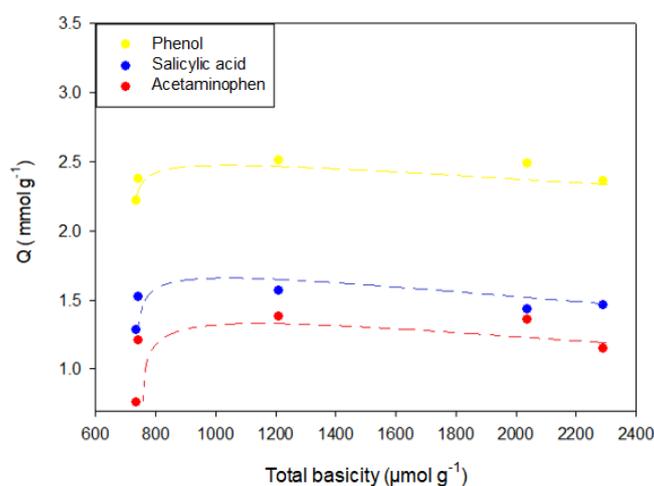


Figure 10. Relationship between the adsorption capacity and the number of basic groups in the adsorption process of phenol, salicylic acid, and acetaminophen on the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

The behavior described in Figure 10 can be explained by the formation of acid-base interactions and the surface charge of the adsorbent. Surface groups such as amines have a pair of free electrons not compromised in the aromaticity of the aromatic rings of the graphene layers, which allows them to interact with Lewis acids such as phenol that could accept a pair of electrons. In the case of oxidized activated carbon, the adsorbed amount of the compound decreases because this adsorbent in solution yields H^+ ions that decrease the pH, which changes the surface charge of the adsorbent. This implies that when the basic groups are protonated, the electronic pair that was free binds to the hydrogen and therefore decreases the amount of groups available to interact with the adsorbate. Likewise, the amount of H^+ ions in the medium interacts with the π electrons of the graphene layers, preventing the formation of adsorbate-adsorbent interactions by π electrons. On the other hand, if the pH of the medium is above the pH at the point of zero charge, the adsorbent will have a negative charge associated with the deprotonation of the acid groups, implying a greater polarity at the surface, which favors the interaction with water. Therefore, as the activated carbons give less H^+ ions to the medium, the adsorption capacity of the pharmaceutical compounds is increased until it remains constant in the reduced activated carbons, which have the same values in the total acidity.

It was found that the adsorption capacity decreases with the molecular weight of the adsorbate, so molecules with higher molecular size may have problems of dissemination and therefore the adsorption depends on the surface chemistry. In the case of acetaminophen, it was envisaged that the surface chemistry of activated charcoal CAO disfavors the process altogether, in part because of the negative charge of carboxylic acids and the increase in the polarity of the surface, which favors the interactions with the solvent.

Methylparaben and acetaminophen have similar molecular weights; therefore, similar to the latter adsorbate, adsorption depends the interactions between the adsorbate and surface groups. However, contrary to phenol, salicylic acid, and acetaminophen, the adsorption capacity of methylparaben increases with the number of oxygenated groups. To analyze the different correlations between the acid groups and the amount adsorbed, it was determined that there is a directly proportional correlation between the amount of acid groups and the adsorbed amount, which can be observed in Figure 11.

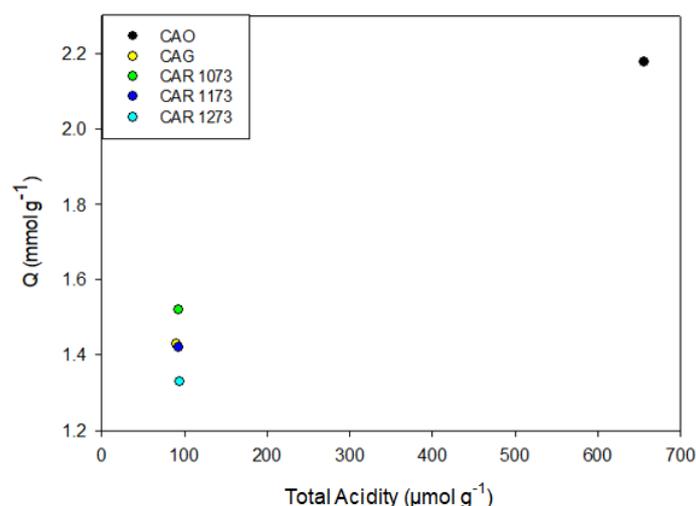


Figure 11. Relation between the adsorption capacity and total acidity on the adsorption of methylparaben on the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

This behavior was attributed to the hydrolysis of the lactone groups in an acidic medium, which form a carboxylic acid and an alcohol after the reaction. This favors the formation of a greater amount of hydrogen bonds with the phenol in the adsorbate structure; likewise, the formation of phenols prevents the solvent from competing for the adsorption sites created, since specific interactions are formed any carboxylic acid-methylparaben and solvent-phenol interactions. As the pH increases, the hydrolysis of the lactones decreases and therefore the adsorption capacity decreases as well. On the other hand, the increase of pH in the medium favors the formation of the dissociated species, generating repulsions with carboxylic acids on the surface.

3.3. Calorimetric Data

In an adsorption system that consists of a solvent, an adsorbate, and an adsorbent, the immersion enthalpy represents the energy exchanged during the interaction of the adsorbate and the solvent with the activated carbon surface. Table 14 shows the immersion enthalpy of activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273 in the solutions of phenol, salicylic acid, acetaminophen, and methylparaben.

Table 14. Immersion enthalpy for the adsorption of phenol, salicylic acid, acetaminophen, and methylparaben in aqueous solution on the activated carbons CAO, CAG, CAR1073, CAR1173, and CAR1273.

Activated Carbon	Adsorbate	Average	Average
		ΔH_{imm} (J g ⁻¹) 0.07–0.66 mmol L ⁻¹	ΔH_{imm} (J g ⁻¹) 1.32–10.2 mmol L ⁻¹
CAO	Phenol	-24.5 ± 1.23	-43.9 ± 0.87
CAG		-9.57 ± 0.48	-34.3 ± 0.69
CAR1073		-15.6 ± 0.78	-36.1 ± 0.72
CAR1173		-10.8 ± 0.54	-35.7 ± 0.71
CAR1273		-29.2 ± 1.46	-23.3 ± 0.47
CAO	Salicylic acid	-27.4 ± 1.37	-35.1 ± 0.70
CAG		-11.3 ± 0.57	38.7 ± 0.77
CAR1073		-31.6 ± 1.58	-36.4 ± 0.73
CAR1173		-11.7 ± 0.59	-37.1 ± 0.75
CAR1273		-21.5 ± 1.08	-29.6 ± 0.59

Table 14. Cont.

Activated Carbon	Adsorbate	Average ΔH_{imm} (J g ⁻¹)	Average ΔH_{imm} (J g ⁻¹)
		0.07–0.66 mmol L ⁻¹	1.32–10.2 mmol L ⁻¹
CAO	Acetaminophen	-33.0 ± 1.65	-56.0 ± 1.12
CAG		-9.83 ± 0.49	-31.9 ± 0.64
CAR1073		-39.0 ± 1.95	39.6 ± 0.79
CAR1173		-9.42 ± 0.47	-34.6 ± 0.69
CAR1273		-23.4 ± 1.17	-24.3 ± 0.49
CAO	Methylparaben	-18.3 ± 0.92	-43.5 ± 0.87
CAG		-11.9 ± 0.56	-51.0 ± 1.02
CAR1073		-41.2 ± 2.06	-42.7 ± 0.85
CAR1173		11.6 ± 0.58	-37.1 ± 0.85
CAR1273		-26.5 ± 1.33	-25.2 ± 0.50

The values in Table 14 indicate that the immersion enthalpy of phenol at low concentrations is highest for activated carbon CAR1273 (although it does not correspond to the greater adsorption capacity). This indicates that, although this surface is hydrophobic, interactions with water can be present through the formation of hydrophobic interactions, which are formed by the creation of water clusters around the carbonaceous surface through hydrogen bonds between them. These strong interactions prevent the interaction of the adsorbate with the adsorbent, even when increasing the concentration. This behavior is repeated for all adsorbates; additionally, it can be seen in Table 14 that the immersion enthalpy values for activated carbon CAR1273 decrease with the increase in adsorbate concentration, indicating that the displacement of solvent from the activated carbon surface requires a very high concentration of adsorbate molecules.

In the case of activated carbon CAO, it was observed that at low concentrations the immersion enthalpy has high values due to the interactions of the adsorbent with the solvent (due to the high polarity of both). The values in the immersion enthalpy increase with the concentration of the adsorbate, indicating that when modifying the concentration of the adsorbate, there is a new equilibrium in which the adsorbate–adsorbent interactions are formed by Le Chatelier’s principle. However, the immersion enthalpy values are associated with solvent–adsorbent interactions, except in methylparaben where they can be associated with adsorbate–adsorbent interactions.

The activated carbons CAG and CAR1173 at low concentrations of adsorbate presented low values of immersion enthalpy due to the competence of the solvent to adsorb the adsorbate through active sites. The increase in the adsorbate concentration increased the immersion enthalpy associated with adsorbate–adsorbent interactions.

4. Conclusions

- An activated carbon prepared from coconut shell was modified by chemical treatment (impregnation with HNO₃) or physical treatment (heating at 1073, 1173, or 1273 K). The oxidation with nitric acid increased the acid groups (656 μmol g⁻¹), but decreased the surface area (469 m² g⁻¹) and micropore volume (0.18 cm³ g⁻¹). On the other hand, the thermal treatment at 1073 K increased the surface area (1127 m² g⁻¹), micropore volume (0.42 cm³ g⁻¹), and the level of basic groups (1270 μmol g⁻¹). The thermal treatment at 1173 and 1273 K decreased textural parameters and increased the basicity.
- The increase of the oxygenated groups in the activated carbon CAO increased the surface polarity, which favored the adsorbent–solvent interactions (water). Using the calorimetric data, it was determined that the immersion enthalpy in water was -66.6 J g⁻¹, while for the activated carbons with thermal treatment the immersion enthalpy in water was -30.4 J g⁻¹.

- It was determined that the adsorption capacity of phenol, salicylic acid, acetaminophen, and methylparaben in the modified activated carbons decreases with increasing the molecular weight of the substituent. For thermally modified activated carbons and CAG, the adsorption capacity decreased by 0.02 mmol g^{-1} per gram of substituent; in the activated carbon CAO, the value decreased by $0.025 \text{ mmol g}^{-1}$ due to the decreases in the pore volume and surface area.
- The adsorption capacity of phenol, salicylic acid, and acetaminophen increased with the basic groups present on the adsorbent. Phenol had the highest adsorption capacities in all activated carbons ($2.28\text{--}2.60 \text{ mmol g}^{-1}$) because it has the smallest molecular size and easy access to micropores. In adsorbates with a larger size, the adsorption capacity depended mainly on the adsorbate-adsorbent interactions. In the case of acetaminophen, the increase in oxygenated groups decreased the adsorption capacity (0.71 mmol g^{-1}) while for methylparaben it increased (2.20 mmol g^{-1}); this was due to the type of interactions that were formed with the adsorbate when it presented an ionic charge, a relevant factor in the adsorption of salicylic acid, which was ionized at the solution pH.
- The immersion enthalpy allowed the association of energy changes in the system with the formation of adsorbate-adsorbent and solvent-adsorbent interactions. Depending on the surface chemistry, the increase of oxygenated groups in the adsorbent increased the immersion enthalpy due to the formation of interactions between activated carbon and water. However, when increasing the concentration of the adsorbate, and increase in enthalpy was observed, which indicated the displacement of the solvent and the formation of activated carbon-adsorbate interactions. The immersion enthalpy values were between -9.42 and -56.0 J g^{-1} .

Author Contributions: V.B., L.G. conceived and designed the experiments; V.B., L.G., and J.C.M.-P. performed the experiments; V.B., L.G., and J.C.M.-P. analyzed the data; V.B., L.G., and J.C.M.-P. wrote the paper; L.G. and J.C.M.-P. critically revised the manuscript.

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