Adsorption of Pharmaceutical Aromatic Pollutants on Heat-Treated Activated Carbons: Effect of Carbonaceous Structure and the Adsorbent–Adsorbate Interactions

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ABSTRACT: Drugs are considered emerging pollutants from water sources and are therefore considered to be of high toxicological risk to aquatic fauna. Activated carbon adsorption is one of the methods approved by the Word Health Organization to remove pharmaceutical compounds from water in treatment plants due to its cost and easy implementation. This study presents the modification of a commercial activated carbon by heat treatment at 1073, 1173, and 1273 K. The impact of the physicochemical changes of the adsorbent on the adsorption capacity of salicylic acid and methylparaben, compounds derived from phenol, was studied. Finally, the adsorbate–adsorbent interactions are evaluated through immersion calorimetry. It is observed that at 1173 K, activated carbon increases its surface area by 29%. At higher temperatures, the surface area drops to 21%. In the activated carbon subjected to heat treatment at 1173 K, it increases the adsorption capacity of salicylic acid and methylparaben by 24 and 34%, respectively, compared to activated carbons subjected to higher temperatures. The interaction enthalpies (adsorbate–adsorbent interaction) have values between −12 and 5 J g−1.

INTRODUCTION

Medicines are chemical compounds designed to diagnose, treat, or prevent diseases and improve the quality of life of humans and animals.1,2 However, practices such as self-medication and improper disposal of partially consumed medicines have led to an increase in pharmaceutical waste.3,4 This has generated the contamination of surface and underground waters and a high toxicological risk for living beings exposed to these compounds.5,6 Currently, components of drug formulations and personal care products are considered emerging contaminants present in waters around the world. This includes tap water for domestic use.7

According to Riva et al., the concentration of drugs in water is low to be considered a risk to humans. However, many of these molecules have high distribution coefficients, indicating their easy accumulation in lipid tissues.8

In animals, these molecules accumulate until reaching concentrations with biological activity in tissues such as the liver, testicles, and kidneys generating irreversible damage to these organs and physiological dysfunctions. Indeed, methylparaben generates cancer and endocrine disruption in aquatic animals.9,10

According to the World Health Organization in the Guidelines for drinking-water quality, water for human consumption should be treated to avoid the consumption of toxins through drinking water. One of the processes endorsed by this organization is adsorption.11 Nowadays, activated carbon adsorption is a method applied in water plants as tertiary treatment to remove pollutants.12

Activated carbon is considered a good adsorbent due to its physicochemical properties such as high porosity, high surface area, and high surface energy; the last one needs to be compensated through the formation of interactions with the adsorbate and the solvent when the system is an aqueous solution.

A part of these characteristics is attributed to the structure of activated carbon, which is made up of disordered graphene layers that form porosity. Associated with these layers are the π-electrons of the aromatic rings; they participate in some interactions very important in the adsorption of pollutants from water especially in ionized species: π−cation, π−anion, and π−
water. However, other interactions will depend on the surface groups.\textsuperscript{13,14}

Some emerging pharmaceutical pollutants contain the structure of the phenolic ring. According to Terzyk and Salame, the main interactions present in the phenolic compound adsorption on activated carbon are $\pi$-stacking, hydrogen bond, ionic interactions, and van der Waals forces.\textsuperscript{15,16}

Typically, the activated carbon surface contains heteroatoms associated with functional groups, which come from the adsorbent starting material. It is observed that the oxygenated groups increase the surface polarity, and thus the interactions with the solvent. To avoid this, activated carbon is subjected to heat treatment between 773 and 1273 K in an inert atmosphere to remove oxygenated chemical groups based on their thermal stability.\textsuperscript{17}

The surface chemistry of activated carbons also determines the heterogeneity of the process and can be described by the Freundlich model (eq 1). This model assumes that the energy exchange of the adsorption is not constant because it is distributed according to the formed interactions with each one of the functional groups (active sites) on the adsorbent. This model has limitations in its use; it is only applicable at low concentrations of adsorbate\textsuperscript{18}

\begin{equation}
Q = K_F C_e^{1/n}
\end{equation}

where $Q$ is the amount of adsorbed drug for each equilibrium concentration ($C_e$), $K_F$ is the Freundlich model constant, and $n$ is a parameter of the model and it is related to the heterogeneity. This model is used in the literature to describe the adsorption of pharmaceutical compounds on activated carbon.\textsuperscript{19–21}

In this work, the adsorption of salicylic acid and methylparaben, pharmaceutical compounds derived from phenol, in activated carbon is studied. The adsorbent, a commercial activated carbon, was heat-treated at 1073, 1173, and 1273 K. The samples were called RAC 1073, RAC 1173, and RAC 1273, respectively.

**Adsorbates.** The main characteristics of reagents used to prepare the solution for the adsorption tests are summarized in Table 2; other chemical characteristics such as $pK_a$, molecular size, and chemical structure are included.

### EXPERIMENTAL SECTION

**Materials. Activated Carbons.** In this study, three activated carbons were used as adsorbents, which were prepared from a commercial activated carbon (GAC) whose characteristics are summarized in Table 1.

#### Table 1. Physicochemical Characteristics of Activated Carbon (GAC)

| precursor          | CARBOCHEM LQ-900S (CARBOCHEM INC.) |
|--------------------|-----------------------------------|
| physical: CO$_2$   | 864 m$^2$ g$^{-1}$                |
| micropore volume   | 0.34 cm$^3$ g$^{-1}$              |
| total basicity     | 742 $\mu$L g$^{-1}$              |
| $pH_{zpc}$         | 5.40                              |
| particle size      | 1–1.5 mm                          |
| iodine number      | 850–950 mg I g$^{-1}$             |
| density            | 50–500 g L$^{-1}$                 |

The activated carbon was immersed in HCl concentration to remove inorganic impurities and then washed with distilled water until a constant pH (6.55) was reached.

Close to 100 g of activated carbon GAC was put in a quartz cell and introduced in a THERMOLYNE F21100 furnace (ThermoFisher) at 1073 K. The ramp of heating was 2 K min$^{-1}$ in a N$_2$ atmosphere. The residence time in the furnace once the temperature was reached was 2 h. Subsequently, the activated carbon was stored in amber glass containers without leaving headspace. This sample was called RAC 1073.

The same procedure was repeated at 1173 and 1273 K. The samples were called RAC 1173 and RAC 1273, respectively.

*Adsorbates.* The main characteristics of reagents used to prepare the solution for the adsorption tests are summarized in Table 2; other chemical characteristics such as $pK_a$, molecular size, and chemical structure are included.

**Table 2. Chemical Characteristics of Phenol, Salicylic Acid, and Methylparaben**

| COMPOUND                  | CHEMICAL                          | $pK_a$ | MOLECULAR SIZE (Å) |
|---------------------------|-----------------------------------|--------|-------------------|
| PHENOL                    | Analytical reagent, Merck - Millipore (Germany) with purity of 99% | 9.99   | 5.76 x 4.17       |
| SALICYLIC ACID            | Analytical reagent, PANREAC (U.S.A) with purity of 99% | 2.97   | 6.96 x 5.87       |
| METHYLPARABEN             | Analytical reagent, PANREAC (U.S.A) with purity of 99% | 8.20   | 8.69 x 5.02       |

The solutions used in the adsorption tests were prepared from a stock solution of 2000 mg L$^{-1}$ equiv to 21.3, 14.5, and 13.1 mmol L$^{-1}$ for phenol, salicylic acid, and methylparaben, respectively. The range of concentrations worked was between 0.07 and 10.6 mmol L$^{-1}$.

All solutions were prepared with distilled and deionized water and stirred at 100 rpm at 293 K. The storage was carried out in amber glass containers away from sunlight.

**METHODS**

*Characterization of Activated Carbons.* The physical and chemical properties of the activated carbons were determined from techniques such as nitrogen adsorption at 77 K and Boehm titration. Next, the procedure performed will be described.
Determination of Specific Surface Area, Micropore Volume, and Pore Size Distribution. Activated carbon between 0.7 and 1 g is weighed and placed in the glass cells (9 mm with filler rod) designed for the AUTOSORB IQ 3 sorptometer (Quantachrome Instruments, Anton Paar). Subsequently, the cell is arranged in the degassing station of the equipment. The equipment was programmed to degas the sample under vacuum conditions at 523 K for 180 min.

Subsequently, the sample was again weighed and placed in the gas adsorption station, inside a Dewar with liquid nitrogen (N$_2$), at 77 K. The adsorption data were adjusted with the Brunauer, Emmett, and Teller (BET) model to determine the surface area, Dubinin–Astakhov (DA) equations for the characterization of micropores, and quenched solid density functional theory (QSDFT) to calculate the pore size distribution.

The procedure was carried out for activated carbons RAC 1073, RAC 1173, and RAC 1273.

Determination of Chemical Groups on the Activated Carbon Surface. The Boehm titrations are a method to determine oxygen surface groups on activated carbon such as phenols, lactones, carboxylic acids, acidity, and total basicity based on the retitration of acids or bases that have been brought into contact with activated carbon.\(^{22}\)

According to the method proposed by Boehm, the use of NaOH solutions serves to determine the total acidity (it titrates carboxylic acids, phenols, and lactones), Na$_2$CO$_3$ to titrate carboxylic acids and lactones, and NaHCO$_3$ to determine the quantity of carboxylic acids.

In this method, 0.5 g of activated carbon is deposited in an amber vessel containing 0.05 L of NaOH/Na$_2$CO$_3$/NaHCO$_3$. We have tried not to leave headspace. Subsequently, it is kept under stirring at 100 rpm and 293 K for 5 days or until a constant pH is reached; this procedure was previously performed.

The amount of each pharmaceutical compound adsorbed (Q) on the adsorbent was determined by mass balance, as shown in eq 2

\[
Q = \frac{(C_0 - C_e)V}{m}
\]

where $C_0$ is the initial concentration, $V$ is the volume used in the tests, and $m$ is the mass of activated carbon.

Calorimetry Tests. A heat-conduction microcalorimeter type Calvet was used in this study. In 1948, Calvet modified Tian’s design by placing two equal systems in an isothermal block (thermostat) where the thermopiles are located between the system and the isothermal block; this allowed to compensate for the fluctuation in the measures and to increase the sensitivity of the equipment.

A sample of 100 mg of activated carbon was put in a glass ampoule with a fragile bottom; the ampoule was placed in the lid and the calorimeter was closed. Previously, 0.01 L of an immersion solution was deposited in a stainless steel cell inside the isothermal block (external metallic coating).

The calorimeter is turned on and the voltage change measurements are obtained as a function of time. Once the baseline is kept constant, the bulb is broken, and the activated carbon comes into contact with the liquid; the voltage recording is continued until returning to the baseline. Finally, an electrical calibration is performed through a resistance coupled to the calorimeter.

To determine immersion enthalpy ($\Delta H_{\text{imm}}$), eqs 3–eq 1 are used

\[
Q_{\text{imm}} = K_{\text{cal}} \times \text{area under curve (immersion peak)}
\]

\[
K_{\text{cal}} = \frac{VIt}{\text{area under curve (calibration peak)}}
\]

\[
\Delta H_{\text{imm}} = \frac{Q_{\text{imm}}}{\text{activated carbon mass (g)}}
\]

where $Q_{\text{imm}}$ represents the immersion heat, $K_{\text{cal}}$ the calorimeter constant, $V$ the voltage, $I$ the electric intense in amperes, and $t$ the calibration time.

The immersion liquids used in this study were water, HCl, and solutions of phenol/salicylic acid and methylparaben at the same concentrations used in adsorption tests.

The different interactions measured by calorimetry are as follows:

\[
\Delta H_{\text{imm}} \text{H}_2\text{O}
\]

Interaction between activated carbon and solvent

\[
\Delta H_{\text{imm}} \text{HCl}
\]

Acid–base interaction: Neutralization of basic groups on activated carbon with acid

\[
\Delta H_{\text{imm}} \text{NaOH}
\]

Acid–base interaction: Neutralization of acidic groups on activated carbon with base

\[
\Delta H_{\text{imm}} \text{DRUG}
\]

Interaction between activated carbon with solvent and pharmaceutical compound
The adsorbate–adsorbent energy ($\Delta H_{int}$) can be obtained by Hess’s Law. For this, the immersion enthalpy of the solvent is subtracted from the immersion enthalpy in drug solution according to eq 6, and the enthalpic contribution of aromatic ring substituents of salicylic acid and methylparaben to adsorbate–adsorbent interactions is calculated from eq 7

$$\Delta H_{int} = \Delta H_{imm, drug} - \Delta H_{imm, H_2O}$$  \hspace{1cm} (6)

$$\Delta H_{intFG} = \Delta H_{int, Drug} - \Delta H_{int, Phen}$$  \hspace{1cm} (7)

## RESULTS AND DISCUSSION

According to the literature, one of the most relevant properties of the adsorption of phenols on activated carbon is the ability of this adsorbent to form interactions by $\pi$-stacking with the phenolic ring of the adsorbates.\textsuperscript{25,26}

According to Lewis’s theory of acid–base reaction, the bases are defined as compounds capable of donating pairs of electrons. Therefore, the activated carbon can be considered a base because it can donate $\pi$-electrons.

The activated carbon basicity can be increased by subjecting the adsorbent to high temperatures as performed by El-Sayed et al. and other authors.\textsuperscript{25,26} Hernández-Monje et al. reported in their study that the basicity of activated carbon increases at temperatures above 973K.\textsuperscript{30}

Figure 1 presents the nitrogen adsorption isotherms at 77 K of RAC 1073, RAC 1173, and RAC 1273. It is observed that the samples have type I (a) isotherms according to IUPAC classification; this shape is typical of microporous materials with low external area. In these materials, a rise in the volume of adsorbed gas at low relative pressures ($P/P^0$) is observed due to the increase in adsorbent–adsorptive interactions in narrow microporosity.\textsuperscript{29}

The pore size distribution was made with QSDFT assuming that the pores are slit/cylindrical, and the results are presented in Figure 2. According to the data, the largest pore volume is between 20 and 30 Å, which confirms that activated carbons are microporous as indicated by the nitrogen adsorption isotherms. It is also observed in Figure 2 that the thermal treatment caused the collapse of porosity greater than 40 Å.

Other physicochemical characteristics of activated carbon samples are characterized to determine the effect of thermal treatment on the physicochemical properties of the starting activated carbon (GAC), and the results are presented in Table 3.

It is observed that the heat treatment between 1073 and 1273 K increases the total basicity of activated carbons; however, it is observed that at temperatures above 1173 K, the physical properties (surface area and pore volume) decrease compared with the values obtained for GAC. This behavior is attributed to the collapse of the carbonaceous structure as reported by Carvajal-Bernal et al. in their investigation. Additionally, the same authors indicated the increase in the crystalline structure in the activated carbons; therefore, there is a rearrangement of the activated carbon structure from disordered layers (origin of the pores) to graphenelike structures.\textsuperscript{27}

Regarding surface chemistry, it was observed that the values of total acidity and quantity of carboxylic acid groups are similar in the three activated carbons. On the other hand, phenolic and lactone groups decrease in activated carbons RAC 1073 and RAC 1173. This behavior is attributed to the thermal stability of the functional groups, which depends on the strength of the bonds and therefore can vary due to inductive effect between the chemical groups adjacent to the group evaluated; hence, the main surface chemical groups on activated carbon have ranges of thermal stability. Shafeyaan et al. determined that the thermal stability of the surface chemical groups on activated carbon varies between 373 and 900 K. Table 4 summarizes the temperatures of thermal stability for the chemical groups determined with Boehm titration.\textsuperscript{40}

The pH<sub>pzc</sub> values show that activated carbons have a positive electric charge at pH less than 8 and a negative electric charge from 8.90, 9.96, and 11.1 for RAC 1073, RAC 1173, and RAC 1273, respectively.

Salicylic acid, methylparaben, and phenol are weak acids; therefore, they partially dissociate in aqueous solutions.

### Table 3. Physicochemical Characteristics of Activated Carbons RAC 1073, RAC 1173, and RAC 1273

| Physical Characteristics | RAC 1073 | RAC 1173 | RAC 1273 |
|--------------------------|---------|---------|---------|
| Surface area (m<sup>2</sup> g<sup>−1</sup>) | 1113 | 814 | 711 |
| Micropore volume (cm<sup>3</sup> g<sup>−1</sup>) | 0.42 | 0.29 | 0.23 |
| Mesopore volume (cm<sup>3</sup> g<sup>−1</sup>) | 0.06 | 0.05 | 0.07 |
| Total volume (cm<sup>3</sup> g<sup>−1</sup>) | 0.48 | 0.34 | 0.30 |

### Chemical Characteristics

| Acidic Characteristics | RAC 1073 | RAC 1173 | RAC 1273 |
|------------------------|---------|---------|---------|
| Total acidity (μmol g<sup>−1</sup>) | 93.6 | 93.0 | 94.1 |
| Total basicity (mmol g<sup>−1</sup>) | 1.21 | 2.04 | 2.29 |
| Carboxylic acid groups (μmol g<sup>−1</sup>) | 66.1 | 66.5 | 64.7 |
| Lactonic groups (μmol g<sup>−1</sup>) | 21.2 | 23.8 | 46.8 |
| Phenolic groups (μmol g<sup>−1</sup>) | 6.36 | 3.71 | 17.5 |
| pH<sub>pzc</sub> | 11.1 | 8.90 | 9.96 |
According to the $pK_a$ value, salicylic acid remains dissociated in most of the pH range, while methylparaben and phenol only have a negative electrical charge at pH greater than 8 and 9.99, respectively.

Once the adsorption tests of the pharmaceutical compounds on activated carbons were carried out, the adsorption isotherms were calculated. The results are shown in Figures 3−5.

The experimental procedure was carried out in water without pH adjustment; due to the chemical variations of the activated carbons, there were changes in the pH of the solution during the adsorption process. The pH values of the solution at initial and equilibrium time are included in Table 5. In parentheses are the percentages of ionized molecules.

Finally, the adsorption isotherms were adjusted to the Freundlich model, and the values of the parameters are shown in Table 6.

Table 6 shows the adsorption parameters of phenol, salicylic acid, and methylparaben found for activated carbon GAC. Regarding the $Q_{0.5}$ parameter, the activated carbon RAC 1073 presents a greater adsorbed amount associated with the improvement in the textural properties due to the heat treatment at 1073 K. Comparing with the activated carbons RAC 1173 and 1273, no significant changes in the amount adsorbed are observed.

In general, the amount adsorbed is proportional to the initial adsorbate concentration; however, this trend is only observed at low concentrations of pharmaceuticals. When the equilibrium concentration of the drug increases, the formation of a plateau is not observed. This behavior can be described by the Freundlich adsorption model. In this model, the formation of lateral interactions is assumed, therefore there is no formation of a plateau. Likewise, the formation of different types of interactions between the adsorbate and the adsorbent, as well as the adsorption in pores with different potentials, leads to the process being considered heterogeneous.

The Freundlich model parameters are $K_F$ and $n$, and $K_F$ is associated with the distribution of the adsorbate between the activated carbon and the concentration of the solution, and $n$ is associated with the relative distribution of energy and intensity of adsorption. The values of $n$ that tend to zero are associated with physisorption, while values close to 1 indicate chemisorption or cooperative adsorption. The values of $n$ indicated that the adsorption is favored by the heterogeneity associated with the surface energy, the adsorbent–adsorbate interactions, and the physicochemical characteristics of the adsorbent.

On the other hand, the adsorption of salicylic acid on the three activated carbons shows values of $K_F$ and $n$ similar to each other. Indeed, the value of $n$ is higher than 0.5, thus the process is considered heterogeneous but it does not have a relation with the adsorption capacity.

The parameter $K_F$ is associated with the distribution of the adsorbate between the activated carbon and the concentration.
in equilibrium. Figure 6 shows the relationship of this parameter with the temperature at which the heat treatment of the activated carbons was carried out.

![Image](image-url)

**Figure 6.** Relationship between $K_F$ and the temperature of thermal treatment of the activated carbons RAC 1073, RAC 1173, and RAC 1273.

In all cases, it is observed that the increase in temperature decreases the $K_F$ constant, an indication of a decrease in the adsorption capacity of activated carbon; an increase of 100 K in the heat treatment temperature of the activated carbons produces a decrease of $K_F$ of 0.006, 0.004, and 0.0017 mmol g$^{-1}$/L mmol$^{-1}$ K for phenol, methylparaben, and salicylic acid, respectively.

It is observed that $K_F$ of the adsorption of salicylic acid does not present a marked slope, which may be associated with a low correlation between heterogeneity and the distribution constant. Freundlich’s model does not allow calculating a maximum adsorption capacity ($Q_m$) of the adsorbate. However, to compare the adsorption capacity ($Q$) for each adsorbate on the three activated carbons the parameter $Q_{0.5}$ was determined. This parameter is the adsorption capacity calculated with Freundlich’s model using 0.5 mmol L$^{-1}$ as the equilibrium concentration.

According to the data in Table 6, the adsorption capacity $Q_{0.5}$ presents the following trend among the studied adsorbates in all activated carbons: phenol > methylparaben > salicylic acid. Therefore, there is no correlation between the amount adsorbed and the molecular size of the adsorbates because methylparaben is larger than salicylic acid.

Additionally, $Q_{0.5}$ increases inversely proportional to the heat treatment temperature to which the activated carbons were treated.

![Image](image-url)

**Figure 7.** Relationship between the (A) surface area and the (B) micropore volume of activated carbons RAC 1073, RAC 1173, and RAC 1273 on the adsorption capacity ($Q_{0.5}$) of phenol, salicylic acid, and methylparaben.

### Table 6. Freundlich Model Parameters for Adsorption of Salicylic Acid, Methylparaben, and Phenol on Activated Carbon RAC 1273 at 293 K

| GAC        | $K_F$ ((mmol g$^{-1}$)/(L mmol)$^{-n}$) | n | $Q_{0.5}$ (mmol g$^{-1}$) | $R^2$ |
|------------|----------------------------------------|---|---------------------------|-------|
| phenol     | 2.25                                   | 0.58 | 1.50                     | 0.98  |
| salicylic acid | 1.34                                   | 0.77 | 0.78                     | 0.99  |
| methylparaben | 1.57                                   | 0.45 | 1.15                     | 0.97  |
| phenol     | 3.44                                   | 0.73 | 2.07                     | 0.96  |
| salicylic acid | 1.44                                   | 0.61 | 0.94                     | 0.94  |
| methylparaben | 2.08                                   | 0.45 | 1.52                     | 0.98  |
| phenol     | 3.11                                   | 0.70 | 1.91                     | 0.96  |
| salicylic acid | 1.17                                   | 0.59 | 0.78                     | 0.98  |
| methylparaben | 1.53                                   | 0.45 | 1.12                     | 0.96  |
| phenol     | 2.21                                   | 0.54 | 1.52                     | 0.97  |
| salicylic acid | 1.09                                   | 0.62 | 0.71                     | 0.96  |
| methylparaben | 1.27                                   | 0.34 | 1.00                     | 0.96  |
subjected. Therefore, the trend of the adsorption capacity \((Q_{0.5})\) for the three activated carbons is RAC 1073 > RAC 1173 > RAC 1273.

Extending the information, the effect of physical properties on \(Q_{0.5}\) was studied. Figure 7A,B shows the relationship between the physical properties of activated carbons and the adsorption capacity of the studied adsorbates. In this figure, a linear trend for the variables is observed, therefore the slope represents the rate of change between them.

The data in Figure 7 show that the adsorption capacity increases with the surface area and the volume of micropores, so that adsorption is favored in activated carbon RAC 1073; likewise, it is observed that the values of \(n\) reached in RAC 1073 are higher than those reported for the other activated carbons when each adsorbate is evaluated individually. Indeed, this behavior is due to the fact that the activated carbon RAC 1073 presents micropores of different sizes, as observed in the pore size distribution (Figure 3), therefore it is expected that adsorption will be a heterogeneous process.

The adsorption capacity \(Q_{0.5}\) increases 1.19 × 10^{-3}, 1.30 × 10^{-3}, and 5.77 × 10^{-4} (mmol m^{-2}) for phenol, methylparaben, and salicylic acid (Table 6). In addition, the same trend is present for micropore volume, and the values for the rate of change are 2.64 mmol cm^{-3} for phenol and 2.79 and 1.24 mmol cm^{-3} for methylparaben and salicylic acid, respectively.

Carvajal-Bernal et al. report the Raman spectroscopy data of the activated carbons RAC 1073, RAC 1173, and RAC 1273. It can be seen that the ratio of the D/G peak intensities decreases with the temperature of thermal treatment. This behavior, according to the authors, indicates that the temperature induces the organization of the graphene layers. This in turn decreases the porosity and adsorption capacity of the adsorbates.\(^{27}\)

The heterogeneity of the process is not only related to the energy potential associated with the pores but also with the pH of the solution and its effect on the ionization of the adsorbates.

The initial pH of the solutions is between 5.9 and 6.90 for methylparaben and phenol; therefore, the concentration of ionized molecules is a maximum of 5%. The pH of the salicylic acid solutions is 2.51 and 30% of ionized molecules.

At these pH values, all activated carbons have a positive charge on their surface due to the protonation of basic groups such as pyrones and nitrogenous groups.

At the end of the adsorption process, the pH of the solutions increased to around 7–8, this is due to an effect of the release of OH^- ions from basic groups on the activated carbon surface or the formation of \(\pi\)-stacking interactions with H^+ ions from the solutions (\(\pi\)-cation/proton adsorption).\(^{31}\)

At these values, the ionization percentage of molecules increases for all adsorbates, especially for salicylic acid where the percentage increases to 99%. Therefore, salicylic acid would be expected to increase its adsorption capacity by formation of ionic interactions with positive charges on activated carbon; however, this behavior is not evidenced in the experimental data.

In accordance with Colominas, Baraza, and other authors, carboxylic acids can form dimers in solution by formation of \(\pi\)-bonds; therefore, the structure of the salicylic acid changes (Figure 8A). As its size increases, it is possible that the steric impedance hinders the adsorption in the micropores.\(^{32,33}\) On the contrary, an increase in the pH solution induces the formation of an ionized molecule (Figure 8B) and an increase of the electron density in the acid function group, thereby decreasing the acidity of the compound and its ability to form an acid-base interaction.

Additionally, the carboxylic acid group on the salicylic acid structure at pH above 5 is deprotonated and forms a negative charge that can delocalize between the carboxylic acid and the alcohol. This negative charge generates repulsive effects with the oxygenated groups on the activated carbon surface such as carboxylic acids (deprotonated).\(^{34}\) The H-bond formation decreases proportionally with the parameter \(n\), as shown in Figure 9.

In Figure 10, the main interaction between phenol and methylparaben with the adsorbent is the formation of H-bonds with the oxygenated groups located at the edge of the micropores.\(^{34}\) Therefore, although methylparaben has 2 proton-accepting groups (versus 1 for phenol), it has a larger size and greater steric hindrance in micropores.

Although the literature reports the importance of the activated carbons’ basicity on the adsorption of aromatic compounds, it is observed that it is not necessarily true, if increasing this parameter decreases physicochemical properties such as surface...
area and micropore volume. Additionally, the basic surface groups can release OH\textsuperscript{−} ions, increasing the pH of the solution, which leads to an increase in the dissociated species and the repulsion forces in the system. An inversely proportional relationship between the basicity of the activated carbons and the amount adsorbed (\(Q_{0.5}\)) is observed in Figure 11.

It is observed in Figure 11 that the increase in the total basicity is inverse to \(Q_{0.5}\) for all adsorbates. The adsorption capacity (\(Q_{0.5}\)) decreases 0.43 mmol of phenol for each mmol of basic groups present on the activated carbon surface. The same trend is found for salicylic acid and methylparaben, and the rate of change is 0.21 and 0.48, respectively.

The immersion enthalpy (\(\Delta H_{\text{imm}}\)) is the result of the energy exchange from the interaction between the solvent and the adsorbent. This thermodynamic parameter is considered a measure of the surface affinity or reactivity of chemical groups on activated carbon to determine the solvent or solution. Table 7 reports the enthalpy data for the immersion of activated carbons in water, acid (HCl), and base (NaOH) solutions.

Table 7. Enthalpy Change for the Immersion of RAC 1073, RAC 1173, and RAC 1273 in Water, HCl, and NaOH Solutions

| Activated carbon | \(\Delta H_{\text{imm}}\) \text{H}_{2}\text{O} (J g\textsuperscript{−1}) | \(\Delta H_{\text{imm}}\) HCl (J g\textsuperscript{−1}) | \(\Delta H_{\text{imm}}\) NaOH (J g\textsuperscript{−1}) |
|------------------|---------------------|------------------|-------------------|
| RAC 1073         | −44.3 ± 3.2         | −54.1 ± 2.1      | −49.5 ± 2.0       |
| RAC 1173         | −52.0 ± 4.5         | −58.9 ± 2.8      | −51.5 ± 1.9       |
| RAC 1273         | −56.1 ± 5.5         | −36.7 ± 1.7      | −23.9 ± 1.5       |

It is observed that the three activated carbons have a similar affinity for water, which is reflected in similar enthalpy values between −27 and −32 J g\textsuperscript{−1}.

The enthalpy change when the activated carbons are contacted with HCl solution is around −50 J g\textsuperscript{−1} for the samples RAC 1073 and RAC 1173; this demonstrates a greater reactivity of the basic groups on these activated carbons than for RAC 1173. Likewise, it is observed that the values of the immersion enthalpy in HCl are higher than those reported for NaOH, indicating the formation of π−cation interactions.

The immersion enthalpy determined for the activated carbons in NaOH solutions shows that the activated carbon RAC 1073 presents a greater reactivity of its acid groups; therefore, it is expected that this adsorbent can form a greater number of van der Waals interactions with the adsorbates. This was corroborated with the adsorption data presented above.

The immersion enthalpy in the solutions of phenol, salicylic acid, and methylparaben was determined. The solutions’ concentrations were 10.8, 7.25, and 6.58 mmol L\textsuperscript{−1} (equivalent to 1000 mg L\textsuperscript{−1}) for phenol, salicylic acid, and methylparaben, respectively. This concentration was selected to conduct the measurements because at intermediate concentrations there are enough adsorbate molecules to induce the displacement of water from the adsorbent surface without adsorbate–adsorbate interactions being prevalent in the system.

Figure 12 shows the correlation between the adsorption capacity \(Q_{0.5}\) and the immersion enthalpy in the working solutions.

In the immersion enthalpy in NaOH solutions, the acid–base interaction between the acid groups on the activated carbon and a strong base is evaluated. When the number of interactions generated is greater, more energy will be released, and therefore the process is exothermic. In Figure 12, it is observed that the immersion enthalpy in NaOH increases inversely proportional to the amount of adsorbed adsorbate. This indicates that the acid groups on the activated carbon are directly involved in the adsorbate–adsorbent interactions due to the fact that as the value of the enthalpy of NaOH increases, the amount of adsorbate adsorbed is greater. This is in line with the hypothesis of the formation of hydrogen bonds as one of the main interactions of the adsorption of the studied compounds. Although salicylic acid exhibits repulsive forces with surface carboxylic acids, other acid groups can interact with it, such as lactones and phenol, which due to their pK\textsubscript{a}s are not deprotonated to the pH values of working solutions.

In Figure 13A, it is observed that the interaction enthalpy values are similar for the activated carbons RAC 1073 and RAC 1173; the enthalpies have values between −10 and −12 J g\textsuperscript{−1}, which indicates that the adsorbate–adsorbent interactions can be the same. In the case of phenol and methylparaben, it is the formation of hydrogen bonds. A slight increase in the interaction enthalpy of salicylic acid on activated carbon RAC 1173 is observed, which is attributed to the formation of π−stacking interactions (π−anion). If this is the case, methylparaben and salicylic acid would have location problems in RAC 1273 activated carbon. Associated with this, for this salicylic acid the negative charge can increase the respiration with the electrons located inside the graphene layers, which can lead to this
adsorbate only being located in the external area of the adsorbent. Indeed, as seen in Figure 13B, the contribution of the carboxylic acid (deprotonation) to the interaction enthalpy is highly exothermic and increases with the basicity of the adsorbent. The energy derived from this interaction (acid–base) does not compensate for the negative effect associated with the decrease in area and porosity due to thermal treatment at temperatures above 1173 K.

The contribution of the ester group to the adsorbate–adsorbent interactions (Figure 13B) presents endothermic values, indicating that the entropic changes associated with the adsorbent interactions (Figure 13B) presents endothermic changes at temperatures above 1173 K.

■ CONCLUSIONS

Thermal treatments above 1000 K are used to decrease the number of oxygenated surface groups and thus decrease the adsorbent surface polarity and increase the adsorbate–adsorbent affinity. Indeed, it is observed that with increasing the temperature of the thermal treatment, the immersion enthalpy in water decreases (−27 J g⁻¹ in RAC 1073 and −31 J g⁻¹ in RAC 1273); however, other factors such as the pH of the solution and ionization of the solutes interfere in the increase of adsorbate–adsorbent interactions.

The energy derived from chemical interactions does not compensate for the negative effects of the porous matrix destruction due to the temperature associated with heat treatment, and therefore the adsorption capacity of phenol, salicylic acid, and methylparaben decreases despite the increase in total basicity of the adsorbent.

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Notes
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