Interaction between Hydrocarbons C₆ and Modified Activated Carbons: Correlation between Adsorption Isotherms and Immersion Enthalpies

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ABSTRACT: Adsorption isotherms of benzene, cyclohexane, and hexane were determined from the gas phase on microporous activated carbons with Brunauer–Emmett–Teller areas between 816 and 996 m² g⁻¹. The Dubinin–Radushkevich equation was used to calculate the parameters of characteristic energy \( E_0 \) and micropore volume \( W_p \). Also, immersion enthalpies of activated carbons in solvents were obtained (benzene: –95.0 to –145.1 J g⁻¹; cyclohexane: –21.2 to –91.7 J g⁻¹; and hexane: –16.4 to –66.1 J g⁻¹), and they were used to calculate the product \( E_0 W_p \) with the Stoeckli and Kraehenbuehl equations. Subsequently, values of \( E_0 W_p \) from the two techniques (between 512 and 2223 J cm³ mol⁻¹ g⁻¹ for the adsorption isotherms; between 1204 and 12008 J cm³ mol⁻¹ g⁻¹ for immersion enthalpies) were correlated with some characteristics of the adsorbate such as molecular size, the molar volume, and the dielectric constant. It was found that modifying the activated carbon affected the adsorption process, being favored by temperature changes and restricted by oxidation processes. The adsorbate, which showed the highest values for \( E_0 W_p \) was benzene, because it had a smaller molecular size and a higher dielectric constant.

INTRODUCTION

Activated carbon is widely used in adsorption processes¹,² and its behavior is closely linked to its porous structure. One of the techniques used for its characterization is the physical adsorption of gases and vapors.³ As activated carbons are mostly microporous, the theory of volume filling of micropores (TVFM)⁴ adequately describes the adsorption on this kind of solid. This theory indicated that if the adsorbate is assumed as a liquid, the fundamental property that determined the adsorption capacity of a microporous solid was the micropore volume, instead of the specific surface.⁵ This theory led to the Dubinin–Radushkevich (DR) model, which allowed one to obtain parameters such as the characteristic energy \( E_0 \) and micropore volume \( W_p \) based on adsorption isotherms.

Another technique to evaluate solid–adsorbate interactions is immersion calorimetry. Immersion enthalpy is a function of the adsorbate and microporous system.⁶ Stoeckli and Kraehenbuehl proposed a mathematical relationship where proportionality between immersion enthalpy and the characteristic energy was shown, and thus a correlation with the microporous system.⁷ This article is interesting since it shows the interaction of three C₆ hydrocarbons with activated carbon, where the adsorbates have different natures: benzene (an aromatic compound), cyclohexane (a closed-chain aliphatic compound), and hexane (an open-chain aliphatic compound). The activated carbons differ in their physicochemical characteristics, mainly in the superficial groups, since these activated carbons have different development of acidity and basicity and they are used to evaluate their behavior as adsorbents of nonpolar substances.

The evaluation of adsorption of these three hydrocarbons had been carried out in materials such as zeolites⁸ and ordered mesoporous carbons,⁹ and some studies were found in activated carbons¹⁰–¹³ where the adsorbed amount was analyzed. However, little was discussed about energy parameters such as characteristic energy of adsorption \( E_0 \) (there was no comparative process and hydrocarbons were evaluated separately¹⁴–¹⁸); the correlation between this \( E_0 \) and the microporous system \( W_p \) was barely addressed and no correlations were found between these two \( (E_0 W_p) \) and the enthalpy of immersion \( (\Delta H_{im}) \). These correlations would be interesting because immersion enthalpy is a thermodynamic parameter that allows us to evaluate the interaction between the adsorbent and the adsorbate, since the works that had been carried out on immersion enthalpies analyzed these compounds separately or maximum two of them (benzene,¹⁹–²¹ cyclohexane,²²,²³ hexane²²,²⁴); also, \( \Delta H_{im} \) is determined by means of immersion calorimetry that is not a conventional technique either. In turn, this paper establishes a relationship...
between the adsorption and immersion process, and the enthalpy values are used to calculate the \( E_oW_o \) parameter by the mathematical equation of Stoeklcki and Kraehnbeuhl, in addition to \( E_oW_o \) previously calculated by the adsorption isotherms through the DR model. Therefore, the aforementioned is a novelty that this manuscript could contribute to this field of research.

### RESULTS AND DISCUSSION

In this manuscript, the relationship between the microporous structure of a solid \((W_o)\), the energy generated by the interaction of an adsorbent when placed in contact with a given adsorbate \((-\Delta H_m)\), and the adsorption energy of the process \((E_o)\) will be established. For this, the mathematical relationship proposed by Dubinin–Radushkevich and Stoeklcki and Kraehnbeuhl was used to calculate the \( E_oW_o \) product by the determination of gas-phase adsorption isotherms and by the immersion enthalpies of activated carbons (with changes in their chemical and textural properties) in three hydrocarbons (benzene, cyclohexane, and hexane). Finally, a correlation between the parameters obtained by the two techniques was established.

**Determination of \( E_oW_o \) by Gas-Phase Adsorption Isotherms and Their Relationship with Physicochemical Characteristics of Activated Carbons.** Characterization of the Porous Solids. Table 1 shows the proximate analysis of samples. As the moisture content is higher in the oxidized samples, the active sites that can interact with the water molecules increases,\(^{25}\) increasing the ability of these porous solids to retain humidity from air. The percentage of volatile matter also increased in samples modified with HNO\(_3\) because groups on the surface of the solid were generated, as well as the humic substances were formed.\(^{26}\) At the same time the fixed carbon of the solids decreased as the volatile material increased; this fixed carbon also increased with the heat treatment temperature since the number of surface groups decreased. Finally, the ash content had similar values; however, the samples CAON, CAON723, and CAON1023 showed a slight detriment. This was because the chemical modification allowed the removal of part of the inorganic matter present in the starting sample.

| sample   | moisture (%) | volatile matter (%) | ashes (%) | fixed carbon (%) |
|----------|--------------|---------------------|-----------|-----------------|
| CAG      | 14.8         | 14.6                | 2.96      | 67.6            |
| CAON     | 17.9         | 23.8                | 1.42      | 56.9            |
| CAON723  | 16.1         | 24.2                | 1.31      | 58.5            |
| CAON1023 | 9.1          | 20.1                | 1.32      | 69.4            |
| CAG1173  | 14.1         | 15.2                | 2.35      | 68.4            |

Table 2 shows physicochemical characteristics of the samples: the apparent surface area and the total pore volume \((W_t)\) obtained by the Brunauer–Emmett–Teller (BET) model, the micropore volume \((W_m)\) calculated by the DR equation as well as the micropore contribution, the average pore size determined from the \( N_2 \) adsorption isotherms by the quenched solid density functional theory (QSDFT) model, the total surface acidity and basicity obtained by Boehm titrations, and the hydrophobic factor \((H_f)\) derived from the relationship between the immersion enthalpies, benzene/water.

According to Table 2, oxidation affected both the porosity and surface chemistry of the original sample. In terms of textural parameters, the apparent surface area, the micropore volume, and the average pore size decreased. With respect to the chemical characteristics, it was observed that the acidic group content practically doubled, and the basicity and hydrophobic character of the activated carbon sample decreased. This occurred because, according to what has been reported, nitric acid increased the amount of superficial oxygenated groups. This favored electrostatic interactions and therefore increased the hydrophobicity of the sample. Furthermore, nitric acid oxidation could cause partial porosity destruction due to erosion of the micropore walls. This decreased the pore volume and it probably generated restrictions on the edges of the graphene layers due to the fixation of these oxygenated groups in the active sites located at the entrance of the micropores. This reduced the amount of adsorbate that was retained in the pores.\(^{27–29}\)

Then, despite having a smaller area, the oxidized sample (CAON) could generate favorable adsorption processes with polar molecules, thanks to the characteristics of its surface chemistry. Due to the fact that the aim of this research was to adsorb hydrocarbons, this sample had the least adsorption capacity and lower values for the adsorbent–adsorbate interaction, which will be demonstrated later.

The other type of modification that was made to the starting sample was thermal treatment at different temperatures. Two of the modified samples were oxidized prior to heating, and the other sample was subjected to thermal modification directly without treatment with nitric acid. It showed that the surface area increased proportionally with the temperature of the thermal treatment.

Table 2 shows that the micropore volume and the average pore size have similar values for all of the samples that were subjected to thermal modifications. This was probably because two processes occurred when oxidation and subsequent thermal treatment were carried out. In the oxidation process, porosity was reduced by the inclusion of surface groups. Later, when the thermal treatment was carried out, some of these surface groups were removed, causing the porosity to increase again. Because the two treatments generated opposite effects, the treated samples had values similar to those obtained for the starting sample.\(^{27–31}\)

| activated carbon | BET surface area \( (m^2 g^{-1}) \) | \( W_o \) \( (N_2-DR) \) \( (cm^3 \ g^{-1}) \) | \( W_t \) \( (N_2-BET) \) \( (cm^3 \ g^{-1}) \) | microporosity \((\%)\) | average pore size \( (N_2-QSDFT) \) \( (nm) \) | total acidity \( (\mu mol \ g^{-1}) \) | total basicity \( (\mu mol \ g^{-1}) \) | hydrophobic factor \((H_f)\) |
|------------------|---------------------------------|---------------------------------|---------------------------------|-----------------|---------------------------------|-----------------|-----------------|-----------------|
| CAG              | 840                             | 0.34                            | 0.38                            | 89.47           | 0.785                            | 195.25          | 83.68           | 2.15            |
| CAON             | 816                             | 0.32                            | 0.37                            | 86.49           | 0.753                            | 392.89          | 54.19           | 1.43            |
| CAON723          | 903                             | 0.35                            | 0.40                            | 87.50           | 0.785                            | 284.86          | 104.95          | 2.02            |
| CAON1023         | 935                             | 0.35                            | 0.41                            | 85.37           | 0.785                            | 62.10           | 263.91          | 3.44            |
| CAG1173          | 996                             | 0.36                            | 0.40                            | 90.00           | 0.785                            | 49.61           | 314.20          | 4.48            |
The corroboration of the addition and subsequent elimination of some surface groups by oxidation followed by heat treatment was shown in the values of total acidity and basicity. CAG had a total acidity of 195.25 μmol g⁻¹, which subsequently increased to 392.89 μmol g⁻¹ for CAON. Therefore, the surface groups such as carboxylic, lactonic, and phenolic groups increased. Later, CAON was subjected to heat treatment at 723 K. This treatment reduced the oxygenated surface groups by approximately 30% (CAON723: 284.86 μmol g⁻¹). At 1023 K, there was a more considerable removal of the acid groups in CAON1023 (62.10 μmol g⁻¹). Finally, the sample subjected to greater heat treatment, but that was not modified with HNO₃ (CAG1173), presented a decrease in the concentration of acidic surface groups by approximately 90% if it was compared with the sample that was oxidized. The removal of these surface groups occurred in the way described above because it was considered that carboxylic groups decomposed between 523 and 673 K, lactones between 673 and 923 K, and phenols between 873 and 1073 K, and temperatures higher than 1173 K decomposed the quinone and pyrone groups. As for the basicity, it was possible that it increased due to the presence of decomposed carboxylic groups. Lactones between 673 and 923 K, and phenols between 873 and 1073 K, and temperatures higher than 1173 K decomposed the quinone and pyrone groups. As for the basicity, it was possible that it increased due to the presence of decomposed carboxylic and pyrone groups that only decomposed at high basicity, it was possible that it increased due to the presence of decomposed quinone and pyrone groups. As for the basicity, it was possible that it increased due to the presence of decomposed quinone and pyrone groups.

The hydrophobic factor showed the consequence of the addition or removal of the surface groups through the modification of samples. CAON had the lowest value (1.43) due to its surface chemistry since it would have a low affinity for nonpolar substances such as these hydrocarbons. When the surface oxygenated groups were reduced due to thermal treatment, the hydrophobic factor increased because there was a greater affinity for nonpolar substances, which made the intensity of the interaction between these hydrocarbons C₆ and the samples higher. CAON had the lowest value (1.43) due to its surface chemistry since it would have a low affinity for nonpolar substances such as these hydrocarbons. When the surface oxygenated groups were reduced due to thermal treatment, the hydrophobic factor increased because there was a greater affinity for nonpolar substances, which made the intensity of the interaction between these hydrocarbons C₆ and the samples higher. CAON had the lowest value (1.43) due to its surface chemistry since it would have a low affinity for nonpolar substances such as these hydrocarbons. When the surface oxygenated groups were reduced due to thermal treatment, the hydrophobic factor increased because there was a greater affinity for nonpolar substances, which made the intensity of the interaction between these hydrocarbons C₆ and the samples higher.

Figure 1 shows the histogram of the pore size distribution of CAG, CAON, and CAG1173. The QSDFT model for mixed slit pore/cylindrical pore geometry was chosen because this determination was also made for the other pore geometries and it showed a lower percentage of error (CAG: 0.97%, CAON: 0.97%, CAON723: 1.10%, CAON1023: 1.61%, and CAG1173: 1.47%). Similar values were evident, as shown by the volume of micropores determined by DR. However, there was a difference for the pore width of 1 nm (CAG: 0.12, CAON: 0.10, CAG1173: 0.14), where the sample subjected to thermal treatment increased its porosity by 24%, while the oxidized sample decreased the pore volume by 14%. The difference was small but it could be generated by the decomposition of the oxygenated groups, as mentioned before.

It was expected that samples with the greatest interaction and the best adsorption capacities for volatile organic compounds (VOCs) were the samples subjected to thermal treatment, given their porosity and surface chemistry. This is corroborated below.

**Determination of Parameters EₒWₒ by Gas-Phase Adsorption Isotherms.** Figure 2 shows the adsorption isotherms of the three hydrocarbons for sample CAON723. The adsorption data have an uncertainty of 1 × 10⁻⁴ mmol g⁻¹. This allowed us to differentiate between adsorption values in the same isotherm and to detect changes in the adsorption of the activated carbons that were studied. It was observed that benzene was the hydrocarbon adsorbed in greater proportion. This could be associated with the molecular size because the adsorbate that had a smaller size would have fewer restrictions to enter the porous structure of the solid. Since benzene was the smallest molecule, it would have greater access to the pores of activated carbon, and therefore more molecules will be adsorbed compared to cyclohexane, which is approximately 30% larger than benzene, and compared to the hexane molecule, which is about twice the size of benzene and had the lowest amount adsorbed.

As the adsorption process occurred mainly in the micropores, it was necessary to characterize these structures. The Dubinin–Radushkevich model is used for the characterization of activated carbon microporosity. This model is based on the theory of volume filling of micropores (TVFM). Here, it was found that micropores seem to be filled with the adsorbate as a liquid due to the adsorption potential. According to TVFM, the Dubinin–Radushkevich (DR) equation is

\[ \log W = \log W_o - \frac{1}{E_o} A^2 \]  

(1)

where \( A = RT \log \frac{p_0}{p} \)  

(2)

A plot of \( \log^2(p/p_0) \) against \( \log W \) fitted a straight line and allowed us to obtain \( W_o \), which is an important parameter to characterize a microporous solid. The value of the slope allowed us to determine the characteristic energy of adsorption \( (E_o) \), which is an energetic parameter to evaluate the adsorption process.
Graphical representations of the DR equation were made to obtain the $E_oW_o$ product. The results shown in Table 3 are consistent with those reported in the literature since published micropore volume values are within the following ranges: benzene, $0.21 - 0.92 \text{ cm}^3 \text{ g}^{-1}$; cyclohexane, $0.11 - 0.69 \text{ cm}^3 \text{ g}^{-1}$; and hexane, $0.19 - 0.70 \text{ cm}^3 \text{ g}^{-1}$.

A directly proportional relationship between the micropore volume and the $E_oW_o$ product is shown in Figure 3. This was because the adsorption in micropores was associated with the adsorption potential that existed within the walls. Also, the increase in the micropore volume implied a greater number of available micropores with a high adsorption potential value. This was a consequence of the superposition of the existing fields in those pores. A similar relationship was observed between the $E_oW_o$ product and the characteristic energy $E_o$.

In Figure 4, an inverse relationship between the molecular size (benzene: $0.37 \text{ nm}$, cyclohexane: $0.48 \text{ nm}$, and hexane: $0.67 \text{ nm}$) and micropore volume is shown; this might be due to the fact that access to the microporous network was more restricted for larger molecules.

### Table 3. $E_oW_o$ Product Obtained from the Graphs of the DR Equation

| adsorbate | sample  | $W_o$ (cm$^3$ g$^{-1}$) | $E_o$ (J mol$^{-1}$) | $E_oW_o$ (J cm$^3$ mol$^{-1}$ g$^{-1}$) |
|-----------|---------|------------------------|---------------------|----------------------------------------|
| benzene   | CAG     | 0.22                   | 5269                | 1146                                   |
|           | CAON    | 0.21                   | 4072                | 839                                    |
|           | CAON723 | 0.23                   | 5917                | 1373                                   |
|           | CAON1023| 0.26                   | 6440                | 1691                                   |
|           | CAG1173 | 0.29                   | 7789                | 2223                                   |
| cyclohexane | CAG     | 0.16                   | 5736                | 913                                    |
|           | CAON    | 0.14                   | 6266                | 852                                    |
|           | CAON723 | 0.18                   | 6326                | 1168                                   |
|           | CAON1023| 0.22                   | 6784                | 1493                                   |
|           | CAG1173 | 0.24                   | 6236                | 1506                                   |
| hexane    | CAG     | 0.07                   | 6881                | 513                                    |
|           | CAON    | 0.07                   | 6922                | 512                                    |
|           | CAON723 | 0.09                   | 6149                | 548                                    |
|           | CAON1023| 0.10                   | 5792                | 572                                    |
|           | CAG1173 | 0.11                   | 5656                | 612                                    |

Figure 3. Relationship between the micropore volume and $E_oW_o$ for activated carbons.

Figure 4 shows that the samples with higher micropore volume were those that were subjected to heat treatment, as this might cause the creation of new micropores or widening of the narrowest pores by the removal of oxygenated groups that had lower thermal stability. This did not occur with the original sample or the oxidized one because they had a higher number of surface groups that limited access of the molecule to the porous structure. Therefore, there was a lower value obtained for the $W_o$ parameter.

Determination of Immersion Enthalpies and $E_oW_o$ Parameter. Immersion enthalpy manifested the interaction between the porous solid with the solvent (benzene, cyclohexane, and hexane). A plot of electrical potential as a function of time was used for the calculation of immersion enthalpy (Figure 5). This plot contained two peaks: the first corresponded to the immersion process and the second to the electrical calibration of the calorimeter. The results of the immersion enthalpies are presented in Table 4.

The results in Table 4 were calculated by the average of three determinations and the standard deviation values are between 0.33 and 2.90 J g$^{-1}$. The immersion enthalpies obtained were exothermic, which was quite consistent with the enthalpies reported in the literature, where $-\Delta H_{imm}$ for benzene presented approximate values between 85 and 176 J g$^{-1}$; cyclohexane between 29 and 102 J g$^{-1}$; and hexane between 31 and 71 J g$^{-1}$. Benzene was the compound with the highest value of enthalpy of immersion, as shown in Figure 6. Contacting benzene with activated carbon involved the interaction of regions with high electron density located in the graphene layers with the $\pi$ electrons of the benzene molecule. The specific interactions between graphenic layers and the aromatic rings of benzene increased when the activated carbon was heat-treated.
Table 4. Immersion Enthalpies of Activated Carbons into Solvents and $E_o W_o$ Product, Determined by the Stoeckli–Kraehenbuehl Equation

| adsorbate | sample | $E_o W_o$ (J cm$^3$ mol$^{-1}$ g$^{-1}$) | $-\Delta H_{im}$ (J g$^{-1}$) |
|-----------|--------|----------------------------------------|--------------------------|
| benzene   | CAG    | 8805                                   | 106.4                    |
|           | CAON   | 7860                                   | 95.0                     |
|           | CAON723| 8929                                   | 107.9                    |
|           | CAON1023| 10659                                  | 128.8                    |
|           | CAG1173| 12008                                  | 145.1                    |
| cyclohexane| CAG   | 5260                                   | 66.0                     |
|           | CAON   | 1693                                   | 21.2                     |
|           | CAON723| 6112                                   | 76.7                     |
|           | CAON1023| 5554                                   | 69.7                     |
|           | CAG1173| 7312                                   | 91.7                     |
| hexane    | CAG    | 3008                                   | 40.9                     |
|           | CAON   | 1204                                   | 16.4                     |
|           | CAON723| 4243                                   | 57.6                     |
|           | CAON1023| 3926                                   | 53.4                     |
|           | CAG1173| 4868                                   | 66.1                     |

Figure 6. Calorimetric curves of CAON1073 in the immersion liquids.

Figure 7 shows the direct relationship between the immersion enthalpy and $W_o$. Martin argues that there was a proportionality between $\Delta H_{im}$ and $E_o$ of the activated carbon, and consequently, a relationship with the microporous system, expressed in $W_o$. Furthermore, Rouquerol et al. mentioned that the interaction between the porous material and the wetting liquid was closely related to the micropore volume. As the micropore volume increased, the affinity between the solid and the adsorbate was favored due to the attractive forces exerted by the activated carbon on the adsorbate. In addition, as mentioned above, the inversely proportional relationship between the molecular size and micropore volume was related to higher values of $W_o$ in benzene. This led to a greater contribution of the adsorption potentials that existed in the micropores, causing a higher adsorbate–adsorbent energy interaction.

Correlation of $E_o W_o$ Parameters. According to the results that were obtained by adsorption isotherms and immersion enthalpies, product $E_o W_o$ was determined in two ways: using the theory of micropore volume filling (TVFM), which provided the DR equation, and the mathematical relationship proposed by Stoeckli and Kraehenbuehl. Then, a relationship between these $E_o W_o$ determinations could be established. Although the values differed, a directly proportional relationship was observed. The difference between the values obtained from the DR equation and the Stoeckli and Kraehenbuehl equation might be related to temperature differences, because the isotherms of the hydrocarbons were determined at 263 K, while the immersion calorimetry of the solids in the solvents was carried out at 293 K. Although a lower temperature favors the adsorption process, the rate of diffusion decreases at low temperatures, especially at lower pressures and mainly in the narrowest pores. This is precisely where the micropore volume filling occurs, as with the nitrogen molecule when the adsorption isotherms are obtained at 77 K.

Figure 8 shows the relationship between $E_o W_o$ obtained by immersion enthalpy as a function of $E_o W_o$, calculated by the adsorption isotherms. This allowed us to establish a relationship between the microporous structure, the adsorption energy related to the adsorption potentials of the walls of such pores, and the molecular interaction between the adsorbate and the activated carbon surface. The highest $E_o W_o$ values were those for the adsorbate with the smallest molecular size and for the samples that were subjected to thermal treatment. The maximum value was for the sample that was modified at the highest temperature (1173 K). Lower values were presented by the oxidized samples.

\[ -\Delta H_{im} = \frac{\beta E_o W_o (1 + \alpha T) \sqrt{\pi}}{2V_m} \]
Finally, the relationship between $E_o W_o$ and the dielectric constant (benzene: 2.27; cyclohexane: 1.99; and hexane: 1.89) was evaluated (Figure 9), since the characteristic energy was related to dispersive forces. The dielectric constant was associated with the degree of polarizability of the molecule. It was found that there was a directly proportional relationship, possibly associated with London dispersion forces, which tended to be stronger between more easily polarizable molecules: $E_o W_o$ product. CAG1173 sample showed the highest values due to two factors: first, because of the heat treatment, the selective removal of several surface functional groups located on the edges of the graphenic layers was performed, allowing more available space for the entrance of the molecules and thus the interaction with the accessible pores, showing higher nonspecific interactions between the adsorbate and the adsorbent; second, this heat treatment favored the presence of delocalized $\pi$ electrons, which could increase the above-mentioned interactions because of the distortion in the organization of electrons, which could generate a greater amount of instantaneous dipole moments, increasing the $E_o W_o$ value. On the other hand, the lower values corresponded to CAON, due to the restrictions for diffusion of the adsorptive liquid on the porous solid caused by the surface oxygenated groups, which had little affinity for the molecules that were adsorbed since these were nonpolar. As a result, this dispersive interaction had lower intensity, decreasing the attractive forces between molecules and the porous network of the activated carbon.

![Figure 8. Correlation of the $E_o W_o$ product obtained by immersion calorimetry and adsorption isotherms.](image)

**CONCLUSIONS**

The modifications made to the activated carbon affected its textural and chemical properties. The oxidation process decreased the surface area, porosity, and the hydrophobic character by increasing the number of oxygenated groups. This disfavored the adsorption process and the energy of interaction between the activated carbon and these hydrocarbons since they were nonpolar molecules. Thermal modification favored the adsorption process because it increased the surface area, porosity, and the hydrophobic character. Increasing the temperature removed oxygenated groups and this improved the affinity between the solid carbon and the VOCs. This was reflected in the amount of VOC adsorbed, the enthalpy of immersion, and the $E_o W_o$ parameters.

![Figure 9. Relationship between the dielectric constant of adsorbates and $E_o W_o$.](image)

![Figure 10. Scheme of the homemade sortometer used to determine the gas-phase adsorption isotherms.](image)
Although immersion calorimetry and the determination of gas-phase adsorption isotherms are different techniques, they provided information about the adsorption process and the microporous structure of the solid. They showed a correlation between the $E_o$ product calculated by the two techniques and its relationship with the limiting adsorption volume of the micropores, the adsorption energy of the system, and the affinity between the adsorbent and the adsorbate.

The thermodynamics of the adsorption process was affected by both the adsorbent and the adsorbate. If the adsorbent was modified, not only was the $W_o$ affected but also the characteristic energy. This occurred because adsorption on the micropores was associated with the adsorption potential contained in the micropore walls. On the other hand, if the adsorbate had a smaller molecular size and a higher dielectric constant, it would favor the adsorption process and increase the energy of adsorption and the adsorbent–adsorbate interaction due to the affinity between the adsorbent–adsorbate and the attractive forces exerted by the adsorbate.

**EXPERIMENTAL SECTION**

**Materials.** A commercial activated carbon prepared from a coconut shell by physical activation (CAG) was used as the starting activated carbon (GS50, Carbochem brand - Carbochem Inc., Philadelphia, PA). The CAG (size: 1 mm) was washed with distilled water and dried at 373 K for 24 h. The activated carbons were stored under a nitrogen atmosphere. Physical and chemical modifications were performed.

**Chemical Modification.** Activated carbon (CAG) was subjected to an oxidation process with a 6 M nitric acid solution (at impregnation ratio of 1:2) at 85 °C for 6 h to obtain the sample (CAON). It was later washed with distilled water and dried at 373 K for 24 h.

**Physical Modification.** CAG was subjected to thermal treatment under a nitrogen atmosphere for 10 h at a rate of 1.5 K min$^{-1}$ and then for 1 h at 1173 K to obtain CAG1173. CAON was also exposed to heat treatment at two different temperatures: for 8 h at a rate of 1.5 K min$^{-1}$ and then for 1 h at 1023 K under a nitrogen atmosphere to obtain CAON1023; and for 5 h at a rate of 1.5 K min$^{-1}$ and then for 1 h at 723 K under a nitrogen atmosphere to obtain CAON723. Thus, five samples were obtained: CAG, CAG1173, CAON, CAON1023, and CAON723.

The thermal treatments were carried out in a Thermolyne horizontal-position furnace with a stainless steel tube with a quartz tube boat. The pyrolysis temperatures were chosen based on the thermal stabilities of the surface functional groups.

**Physicochemical Characterization. Nitrogen Adsorption Isotherms.** Nitrogen adsorption isotherms were obtained using an Autosorb 3B, Quantachrome at 77 K, to determine the apparent surface area using the Brunauer–Emmett–Teller (BET) model, the micropore volume and characteristic energy using the Dubinin–Radushkevich (DR) model, and the pore size distribution by applying quenched solid density functional theory (QSDFT) analysis. The samples were previously degassed at 473 K for 24 h.

**Boehm Titrations.** These were used to determine the content of oxygenated groups on the activated carbons, evaluated through the total acidity and basicity of samples.

**Total acidity.** One hundred milligrams of activated carbon were mixed with 25 mL of 0.1 M NaOH solution. This mixture was stirred for five days at 293 K. Ten milliliters of each solution in contact with the solid were titrated with previously standardized HCl solution.

**Total basicity.** One hundred milligrams of activated carbon were mixed with 25 mL of 0.1 M HCl solution. The mixture was stirred for five days at 293 K. Ten milliliters of each solution in contact with the solid were titrated with previously standardized NaOH solution.

The titrations were performed using a TitroLine α plus titrator from Schott Instruments.

**Proximate Analysis.** Proximate analysis for the determination of moisture, volatile matter, and ashes of the samples was performed according to ASTM standards. The fixed carbon content was determined by the difference from the other tests.

**Determination of Gas-Phase Adsorption Isotherms.** The adsorption isotherms were determined in a sorotometer assembled in the laboratory (Figure 10). Three adsorptive liquids were used: benzene, cyclohexane, and hexane. The adsorptive liquid was placed in a stainless steel cell with a capacity of 5.0 mL. Then, it was passed through a stainless steel pipe and kept in a tank (an autotransformer was used to keep the tank at a constant temperature of 343 K), where, by the increase of the temperature it reached its vapor phase.

For solid degassing, 1.000 g of sample was weighed into a glass cell, then placed in the sorotometer, and introduced into an oven connected to an autotransformer to regulate the temperature (423 K); degassing was complete when the pressure value was reached and then the valve was closed. The data collection was done by software that captured 19601

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which was fitted with a stainless steel cell that contained 10 mL of solvent. One hundred milligrams of activated carbon were weighed in a glass vial and placed in the calorimeter cell. The output electric potential was recorded for approximately 40 min until a stable baseline was reached with a variation of about $2 \times 10^{-6}$ V. Later, the sample was immersed into the solvent, and the electric potential increase was recorded until the baseline was attained again. Then, the electrical calibration of the calorimeter was performed $^{68,69}$.

The characteristics of the chemicals that were determined are shown in Table 5.

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**Author Contributions**

D.H.-M., L.G., and J.C.M.-P. conceived and designed the experiments; D.H.-M. performed the experiments; D.H.-M., L.G., and J.C.M.-P. analyzed the data; L.G. and J.C.M.-P. contributed reagents, materials, and analysis tools; D.H.-M., L.G., and J.C.M.-P. wrote the paper. This manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript. D.H.-M., L.G., and J.C.M.-P. authors contributed equally.

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**ABBREVIATIONS**

$E_c$:characteristic energy; $W_m$:micropore volume; TVFM:theory of volume filling of micropores; CAG:starting activated carbon; CAG1173:starting activated carbon that was exposed to an oxidation process with a 6 M nitric acid solution; CAON723:oxidized carbon exposed to heat treatment at 723 K for 5 h under a nitrogen atmosphere; CAON1023:oxidized carbon exposed to heat treatment at 1023 K for 8 h under a nitrogen atmosphere; BET:Brunauer–Emmett–Teller; DR:Dubinin–Radushkevich; QSDFT:quenched solid density functional theory; $H_{imm}$:immersion enthalpy; $H_f$:hydrophobic factor; VOCs:volatile organic compounds; $p_s$:saturation pressure; $p$:equilibrium pressure; $p^0/p$:relative pressure; $\beta$:affinity coefficient; $\alpha$:thermal expansion coefficient of the liquid; $V_m$:molar volume of the liquid

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