# Preparation and Characterization of Carbons from Coffee Residue: Adsorption of Salicylic Acid on the Prepared Carbons

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Five activated carbons were prepared at 600 °C from coffee residue by chemical activation using $ZnCl_2$. The effects of the impregnation ratio ($ZnCl_2$/coffee residue) varying from (0 to 100) % on the physical and chemical characteristics were studied. Characterization of these samples was performed by using thermogravimetric analysis, scanning electron microscopy, Fourier transform infrared spectroscopy, and nitrogen adsorption−desorption isotherms at 77 K. Results showed that the microporosity ($V_{mic}/V_{tot}$) presented by the activated carbon at 25 % was more important with 95.70 %, while the other results indicated (92.33, 81.55, and 70.04) % for the rest of activated carbons prepared with activation ratios of (50, 75, and 100) %, respectively. Other physical and chemical characteristics such as $pH_{PZC}$, apparent and real density, and so forth were also determined to complete the characterization. All of the prepared carbons were subjected to the adsorption of salicylic acid. The obtained results showed that the adsorption of salicylic acid is more effective onto activated carbon prepared with 25 % of $ZnCl_2$ (AC 25 %). Consequently, the results of this study show that the coffee residue can be converted into activated carbon with desired characteristics by a judicious choice of activation ratio.

## 1. Introduction

Currently, water pollution is a major problem that has received much attention from both scientists and politicians. There are many industrial wastes containing organics which are difficult to remove by conventional biological treatment processes. However, there are many methods such as oxidation, precipitation, ion exchange, and solvent extraction which can resolve the problem. However, the most widely used method is adsorption onto activated carbon. It removes many of the impurities occurring in water and wastewater.[1]

However, the high cost of this product has caused economical problems. Consequently, interest has focused on the exploitation of environmental wastes with high carbon content. Besides eliminating environmental pollution, it can provide a new and low cost activated carbon.[1]

Environmental wastes are important as starting materials for the preparation of activated carbon. The qualities and the characteristics of the activated carbon (AC) depend on both the chemical and the physical properties of the starting materials and activation methods. Depending on the physical aspect, activated carbon can be produced in three forms: powder activated carbon (PAC), granular activated carbon (GAC), and fibrous activated carbon (ACF). Concerning the activation, there are basically two methods: physical and chemical activation. The first one, called also thermal activation, is carried out in two steps: pyrolysis of the starting material and activation of the char by using carbon dioxide or steam. On the contrary, the chemical method requires only one step. The precursor is impregnated with an activating agent ($ZnCl_2$, $Na_2CO_3$, $K_2CO_3$, KOH, NaOH, $H_3PO_4$, $H_2SO_4$, etc.) and, then, is heated under an inert atmosphere ($N_2$, Ar, or $CO_2$). This method occurs at lower temperature than that of the physical methods. Therefore, it improves the pore development in the carbon structure. The type of chemical agent is selected as a function of the characteristics of the desired activated carbon, that is, KOH produces only widening of the microporosity to more heterogeneous micropores, whereas $ZnCl_2$ develops both wide micropores and low mesopores and $H_3PO_4$ develops large mesopores and even macropores.[2]

Chemical activation using $ZnCl_2$ has been studied by several researchers using different preparation conditions. This chemical is used to dehydrate the starting material and to retard the formation of tars during the activation and the carbonization process.[3]

This paper describes the preparation of an activated carbon produced by coffee residue through chemical activation using $ZnCl_2$. Moreover, some characteristics of this product were determined by means of physical and chemical analysis methods.

## 2. Materials and Methods of Characterization

***2.1. Materials.*** The precursor used is coffee residue which was collected in coffee houses and households. Zinc chloride and salicylic acid of purities 95 % and 99.5 %, respectively, were obtained from BIOCHEM Chemopharma.

***2.2. Preparation of Adsorbents.*** To obtain an activated carbon, several treatments were carried out on the material, and the general schematic diagram for the preparation has been given in Figure 1.

The waste was washed to remove impurities and dried. The residue was subjected to chemical activation using $ZnCl_2$ with different activating ratios: (0, 25, 50, 75, and 100) %. The reagent was dissolved in hot water (85 °C) and mixed with the precursor. The mixture was put in an oven at 85 °C for 7 h to facilitate the hydration of the precursor and the swelling of the internal channels of the lignocellulosic structure allowing for better access of the $ZnCl_2$ into the interior of the particles. The temperature was raised to 110 °C, and the mixture was kept

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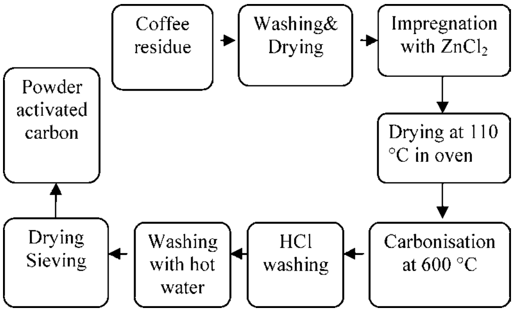

**Figure 1.** Schematic presentation for preparation of activated carbon from coffee residue.

for 24 h at this temperature to cause complete evaporation of the water, facilitating the incorporation of $ZnCl_2$ into the interior of the particles.

The precursor was subjected to the carbonization at a heating rate of 10 $°C\cdot min^{-1}$ under nitrogen flow and held at 600 °C for 1 h. The resulting carbon was treated with HCl solution (10 %) to remove the impregnation salt followed by washing with hot distilled water (65 °C) to remove the acidity of the carbon and chlorides. The washing operation is stopped when the conductivity of the washing water reached the conductivity value of the distilled water used ($\approx 7\ \mu s\cdot cm^{-1}$). The resultant activated carbon was dried and ground to particles having an average size of 63 $\mu$m. The activated carbons obtained in this way were designated as (AC 0, AC 25, AC 50, AC 75, and AC 100) %, taking into account the activating ratios.

***2.3. Thermogravimetric Analysis (TGA).*** Thermogravimetric experiments were carried out by a thermogravimetric analyzer (SETARAM; TG DTA 92) to determine the pyrolysis behavior of the coffee residue and $ZnCl_2$ impregnated coffee residue. Coffee residue, $ZnCl_2$, and $ZnCl_2$ impregnated coffee residue were subjected to the following experimental conditions: ambient temperature of 600 °C at a heating rate of 10 $°C\cdot min^{-1}$ under nitrogen gas flow for 1 h.

***2.4. Surface Chemistry Determination. 2.4.1. $pH_{PZC}$ Determination.*** The pH of the point of zero charge ($pH_{PZC}$) of the carbon sample was determined using the method reported by Villacañas et al.[4] Aliquots with 50 mL of 0.01 M NaCl solution were prepared in different flasks. Their pH values were adjusted between 2 and 12 with the addition of 0.01 M solution of HCl or NaOH. A 0.15 g portion of the carbon was added to each flask and shaken for 48 h. When the pH value remained constant, the final pH was measured using a pH meter. The $pH_{PZC}$ value is the point where the curve $pH_{final}$ versus $pH_{initial}$ crosses the line, that is, $pH_{initial} = pH_{final}$.

***2.4.2. Boehm Titration.*** Boehm titrations[5] are one of the most widely used methods to quantify acidic groups with different strengths on activated carbons. It was used initially for the differentiation of oxygen-containing groups. In this study, it was assumed that 0.1 N sodium bicarbonate ($pK_a = 6.37$) only neutralizes strong acidic groups (both carboxylic- and phosphorus-containing groups), 0.1 N sodium carbonate ($pK_a = 10.25$) neutralizes both strong and intermediate acidic groups, and 0.1 N sodium hydroxide ($pK_a = 15.74$) neutralizes weak acidic groups as well as intermediate and strong acidic groups. During the analysis, 0.2 g of the carbon sample was mixed with 50 mL of 0.1 N base solution in a 250 mL Erlenmeyer flask. The flasks were sealed and shaken for 48 h at 150 rpm before filtration. Ten mL of the filtrate was pipetted, and the excess base or acid was titrated with HCl (0.1 N) or NaOH (0.1 N), respectively. The number of acidic sites was determined with the assumption that NaOH neutralizes acidic groups, and the number of basic sites was determined from the amount of hydrochloric acid that reacts with the carbon.

***2.4.3. Infrared Spectroscopy.*** The nature of surface groups of activated carbons was performed by IR analysis. Fourier transform infrared (FTIR) transmission spectra of carbon samples were obtained using the potassium bromide technique[5] on a FTIR spectrometer over the wavenumber range of (4000 to 400) $cm^{-1}$. Carbon powder was mixed with potassium bromide at a ratio of roughly 1/1000.

***2.5. Morphology of Activated Carbons.*** The five activated carbons were analyzed by using a scanning electron microscope to study the morphologies of the different activated carbons.

***2.6. Activated Carbon Texture Characterization.*** The structural heterogeneity of the carbons was characterized by $N_2$ adsorption−desorption isotherms measurements at 77 K using a QUANTACHROME NOVAWIN2 analyzer to determine the specific surface area and pore volume of the samples (coffee residue and five activated carbons with different impregnation ratios, i.e., (0, 25, 50, 75, and 100) %). The specific area ($S_{BET}$) was calculated by the BET method. The total pore volumes were estimated on the basis of the liquid volume of nitrogen adsorbed at a relative pressure of 0.98. The microporous volumes (pores < 2 nm) (IUPAC, 1985) were determined according to the Dubinin−Radushkevich equation (DR plots):[6]

$$\log_{10}V_p = \log_{10}V_{mic} - D[\log_{10}(P_0/P)]^2$$

where $P_0$ is saturation pressure, $D$ is constant, and $V_{mic}$ is the total micropore volume.

The microporous volume ($V_{mic}$) and the external surface ($S_{ext}$) were obtained by the $t$-plots method. The microporous surface area ($S_{mic}$) was calculated by subtracting the external surface area from the BET surface area.[7]

The mesoporous volume ($V_{mes}$) was obtained by deducing the microporous volume from the total volume.

The average pore diameters were deduced from $S_{BET}$ and the total volume ($dp = 4V_{tot}/S_{BET}$).

***2.7. Adsorption of Salicylic Acid.*** To evaluate the performance of the prepared carbons from coffee residue, adsorption test experiments were carried out by putting in contact 1 g of carbons with 1 L of salicylic acid solution (30 $mg\cdot L^{-1}$, pH = 3) at ambient temperature. The experiments were undertaken in a batch system. The evolution of the adsorbed quantities of salicylic acid was evaluated using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m}$$

where $q_t$ is the adsorbed amount of the salicylic acid at time $t$, $C_0$ and $C_t$ are initial and final salicylic acid concentrations, respectively, $V$ is the volume (L) of the salicylic acid solution, and $m$ is the carbon mass (g).

The percentage of salicylic acid removal ($R$) is calculated using the following relationship:

$$R(\%) = \frac{C_0 - C_t}{C_0}\cdot 100$$

## 3. Results and Discussion

***3.1. Thermogravimetric Analysis (TGA, DTG, and DTA).*** Figure 2a−c shows the thermal decomposition in a nitrogen atmosphere at a 10 $°C\cdot min^{-1}$ heating rate of the coffee residue (Figure 2a), $ZnCl_2$ (Figure 2b), and impregnated coffee residue at a ratio of 1:4 $ZnCl_2$ to coffee residue by weight (Figure 2c).

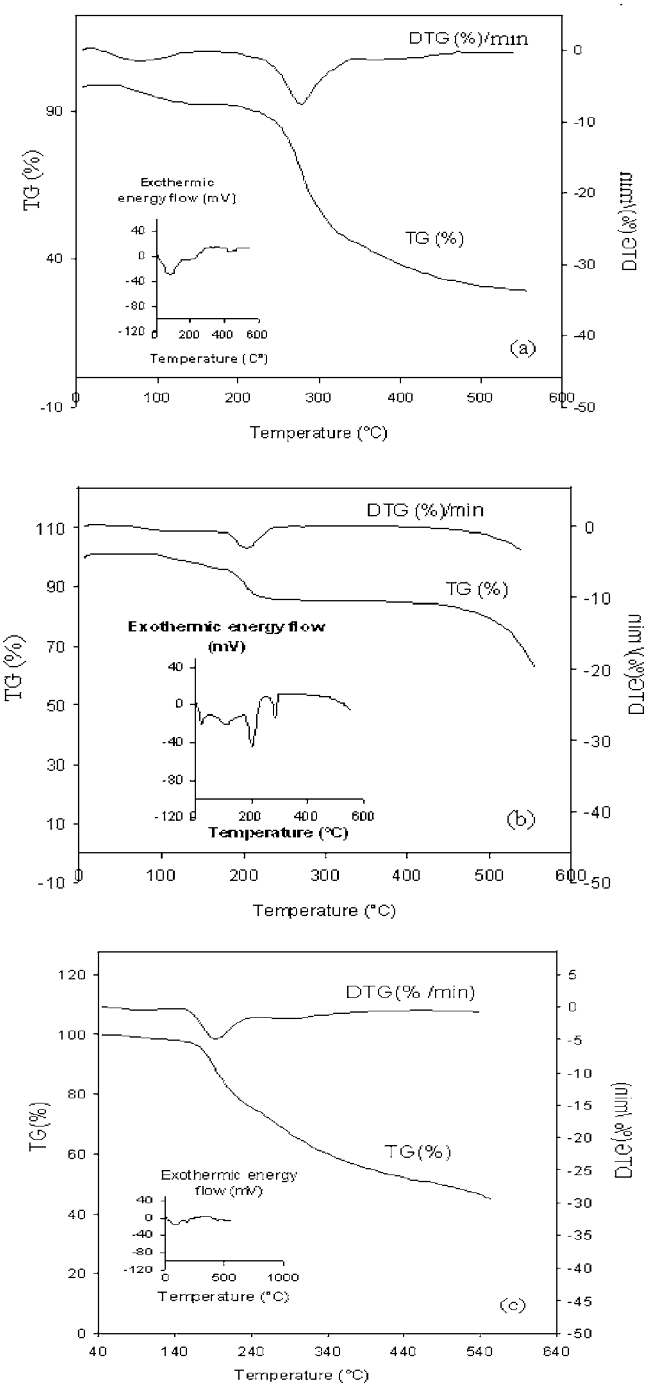

**Figure 2.** TGA, DTG, and TDA curves of (a) coffee residue, (b) $ZnCl_2$, and (c) $ZnCl_2$ impregnated coffee residue (AC 25 %).

Figure 2a shows that the thermal decomposition behavior of the coffee residue is as follows:

In the range of ambient temperature to 125 °C, a small amount of weight loss in the TG curve was recorded, accompanied by peaks in the differential thermogravimetry (DTG) and differential thermal analysis (DTA) curves at 75 °C corresponding to the release of moisture, which saturated the material during its storage. The next range, going from (200 to 600) °C, presents a significant weight loss accompanied by a large peak in the DTG and DTA curves at 280 °C due to the decomposition of coffee residue and its transformation to volatiles ($H_2O$, CO, $CO_2$, $CH_4$, etc.). The degradation continues between (350 and 400) °C assigned to the distillation of tar and the weight loss in a broad manner measured until 600 °C, indicating that the basic structure of carbon was readily formed.[8]

**Table 1. Surface Groups of Activated Carbons**

| carbon | acidic function mmol·$g^{-1}$ | basic function mmol·$g^{-1}$ | acidic func/basic func |
|---|---|---|---|
| non-activated (0 %) | 4.30 | 0.40 | 10.75 |
| AC 25 % | 3.30 | 1.70 | 1.94 |
| AC 50 % | 3.44 | 1.40 | 2.46 |
| AC 75 % | 3.75 | 0.99 | 3.79 |
| AC 100 % | 3.58 | 0.32 | 11.18 |

Figure 2b represents $ZnCl_2$ (TG, DTG, and DTA) thermograms showing three stages of thermal decomposition. The first one presents a small weight loss registered at $T < 120$ °C, assigned to the evaporation of free water imprisoned in the material and revealed by small DTG and DTA peaks in this region. The second one is attributed to the decomposition of $ZnCl_2$ represented by a small amount of weight loss (TG) characterized by peaks of DTG and DTA at 209 °C. The last one spread to 600 °C, corresponding to a phase transformation represented by a plateau for both the TG and the DTG curves and accompanied by an energy consumption indicated by the DTA curve at 286 °C which corresponds to the $ZnCl_2$ melting point. A weight loss was registered at about 500 °C.

Concerning the $ZnCl_2$/coffee residue mixture, two stages of thermal decomposition were observed in the thermal analysis (Figure 2c). At the beginning, a release of moisture was recorded from ambient temperature and 125 °C, indicated by a DTA peak much lower than those corresponding to the untreated coffee residue which proves the desiccant effect of $ZnCl_2$. From (200 to 400) °C, a gradual weight loss appeared in the TG curve because of the pyrolysis of the residue in the mixture. As $ZnCl_2$ underwent little weight loss at this stage, the existence of this agent in the mixture presents a significant effect on the decomposition of the residue because, in addition to its desiccating effect, it has a restriction action in the formation of tar, since the DTA and DTG peaks corresponding to the formation of tar and volatiles were practically absent. The DTG at 209 °C corresponds to the $ZnCl_2$ decomposition. From (400 to 600) °C, there was a weight loss contributing to the release of both $ZnCl_2$ and a few volatiles. Then, the carbon structure was readily formed.[9]

It can be concluded that the addition of $ZnCl_2$ has a significant effect on the decomposition of the precursor by desiccating it at low temperature and restricting the formation of volatiles and tar. In addition, the main role of this agent is to create the porosity of the activated carbon, since the activation occurs at 400 °C, slightly higher than the $ZnCl_2$ melting point of 286 °C, revealing that the higher porosity could be created from the spaces left by the chemical agent after the acid washing.[9]

***3.2. Chemical Characterization. 3.2.1. Boehm Titration Results.*** Besides porosity, the adsorption behavior of activated carbon is also influenced by the chemical reactivity of the surface. The results obtained are presented in Table 1.

According to the results, the non-activated carbon presents the higher content of acidic groups (4.3 mmol·$g^{-1}$). The prepared activated carbons exhibit practically the same content of acidic groups because the values oscillate between (3.3 and 3.75) mmol·$g^{-1}$. Concerning the basic groups, the carbon prepared with an impregnation ratio equal to 25 % has the highest basic group content (1.7 mmol·$g^{-1}$), and the one having an impregnation ratio equal to 100 % has the lowest content (0.32 mmol·$g^{-1}$).

The ratio of the acidic function to the basic function gives information about the acidity rate of the prepared carbons. The

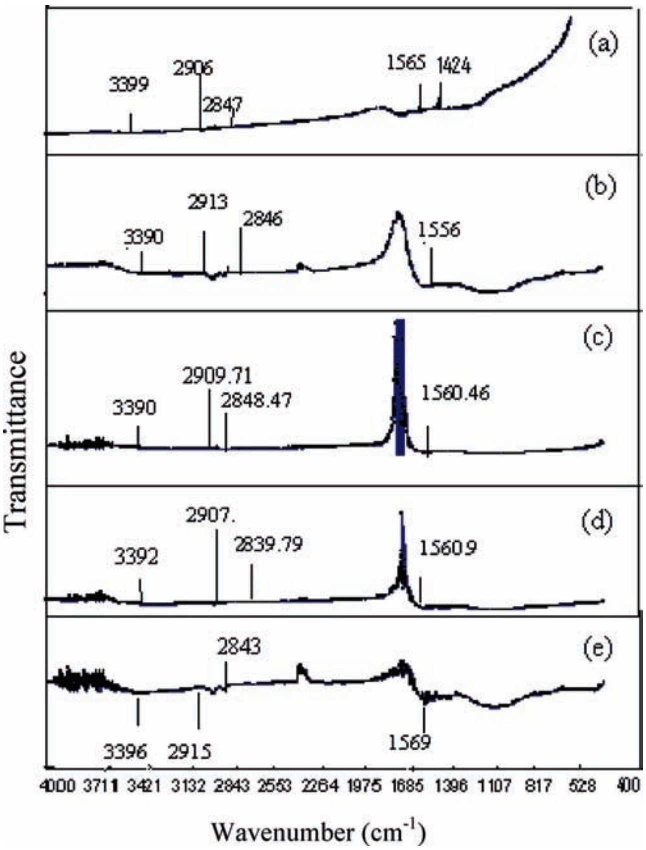

**Figure 3.** FTIR spectra of the prepared carbons (a) non-activated (0 %), (b) AC 25 %, (c) AC 50 %, (d) AC 75 %, and (e) AC 100 %.

larger this ratio is, the higher the acidity of the carbon. This parameter is very useful in adsorption interpretation.[9]

***3.2.2. FTIR Analysis.*** The FTIR spectra of the non-activated carbon and the prepared carbons with different ratios [(25, 50, 75, and 100) %] are shown in the Figures 3a−e.

The spectrum for the non-activated carbon (Figure 3a) displays the following bands:

1. The band at 3399 $cm^{-1}$ is the OH group of the phenol function.[10]
2. The absorption bands observed in the area of (3100 to 3600) $cm^{-1}$ correspond to the vibration of hydroxyls fixed on the surface of carbon and water chimisorbed on carbon.[11]
3. Bands at 2906 $cm^{-1}$ and 2847 $cm^{-1}$ correspond to stretching C−H groups, and they represent aliphatic, olefinic, and aromatic structures. The first one could correspond to bands of $CH_2$− groups, while the second one to −O−$CH_3$ or two bands of aldehyde groups.
4. The band at 1565 $cm^{-1}$ is the C═O stretch of the carbonyl group in a quinone and represents the $\gamma$-pyrone structure with strong vibrations from a combination of C═O and C═C.[10]
5. The band at 1424 $cm^{-1}$ is the C−O stretch or O−H deformation in carboxylic acids.[12]
6. The band at 1249 $cm^{-1}$ could correspond to ketones, alcohols, pyrones, and aromatic C−H in-plane deformations.[13]
7. The absorption around (1000 to 1350) $cm^{-1}$ could be related to the existence of the C−O single bond in carboxylic acids, alcohols, phenols, and esters.[13]

The spectra of the prepared activated carbon, AC 25 %, AC 50 %, AC 75 %, and AC 100 %, display practically the same functional groups found in the AC 25 %. The difference is in the intensity of the peaks. The presence of hydroxyl groups of phenolic and carboxylic character causes acidic surface properties, whereas carbonyl and quinone groups bring about surface basicity. Hence, all prepared activated carbons exhibit both acidic and basic surface functional groups.

One can notice the presence of large bands located between (3600 and 3700) $cm^{-1}$, formed by several peaks of less intensity which could be attributed to free OH (humidity).

***3.3. Morphology of Activated Carbons.*** The analysis of microstructures of the prepared activated carbons is shown in Figure 4a−f, which presents scanning electron micrographs for different activating ratios. The obtained micrographs detail the morphology of each carbon. It is noticed that the porous structure (size of the pores) is well-developed, containing different sizes and shapes of pores which result from the activation process. Subsequently, the higher the activating ratio is, the more important the porosity is. The existing layers within the structure which include small pores are noticed in the non-activated carbon (Figure 4a), and they are gradually enlarged with the activating ratio (Figures 4b−e). It could be attributed to the $ZnCl_2$ action; $ZnCl_2$ is a dehydrating agent which may alter the pyrolysis behavior of the carbonaceous material. After mixing with carbon material, $ZnCl_2$ can be intercalated in the carbon matrix. Upon pyrolysis, a rigorous interaction between the zinc compounds and the carbon atoms occurs. Therefore, atomic layers of carbon may be widened, and pores may be formed in the carbon matrix. During the pyrolysis, $ZnCl_2$ causes hydrogen and oxygen atoms to be removed from the source materials as volatiles or liquid phase, and then more pores are created.[14] White spheres which are observed on the micrographs may be due to the presence of minerals and some other impurities.

***3.4. Activated Carbon Texture Characterization. 3.4.1. Nitrogen Isotherm and Surface Area.*** Figure 5 shows $N_2$ adsorption−desorption isotherms of the prepared activated carbons from coffee residue including the precursor. The amount of nitrogen adsorbed onto the different adsorbents is plotted against the relative pressure $P/P_0$; $P$ is the vapor pressure, and $P_0$ is the saturated vapor pressure of the gas. The lower branch of the isotherms represents measurements obtained by progressive adsorption of $N_2$ onto the adsorbents, while the upper ones are linked to progressive gas desorption.

The $N_2$ adsorption−desorption isotherm corresponding to the coffee residue is type II related to non-microporous solids.[12]

The obtained results show that the AC 100 %, AC 75 %, AC 50 %, and AC 25 % exhibit the same shape. They are type I with a small hysteresis loop of type $H_4$, according to the IUPAC classification. They are characteristic of microporous solids.[8]

The adsorption curve rises sharply at relative pressure of $P/P_0$ less than 0.2 and then approaches a plateau with increasing relative pressure. The adsorption and the desorption branches are parallel over a wide range at higher relative pressure, indicating the highly narrow pore size distribution of the microporous materials with slit-like or plate-like pores.

Boudrahem et al.[3] have prepared carbons from coffee residue impregnated by zinc chloride using the same conditions to treat water contaminated by lead. The carbon characteristics reported are different to those obtained in the present paper. These differences can be explained by the fact that the used coffee residue was collected in coffee houses and households continually, and consequently, the properties of this residue may be different (ratio of Arabica, Robusta.). Ioannidou and Zabanitou[15] have reported in their review that the differences in the ultimate and elemental analysis of activated carbons produced from different raw materials, under the same conditions, indicate the

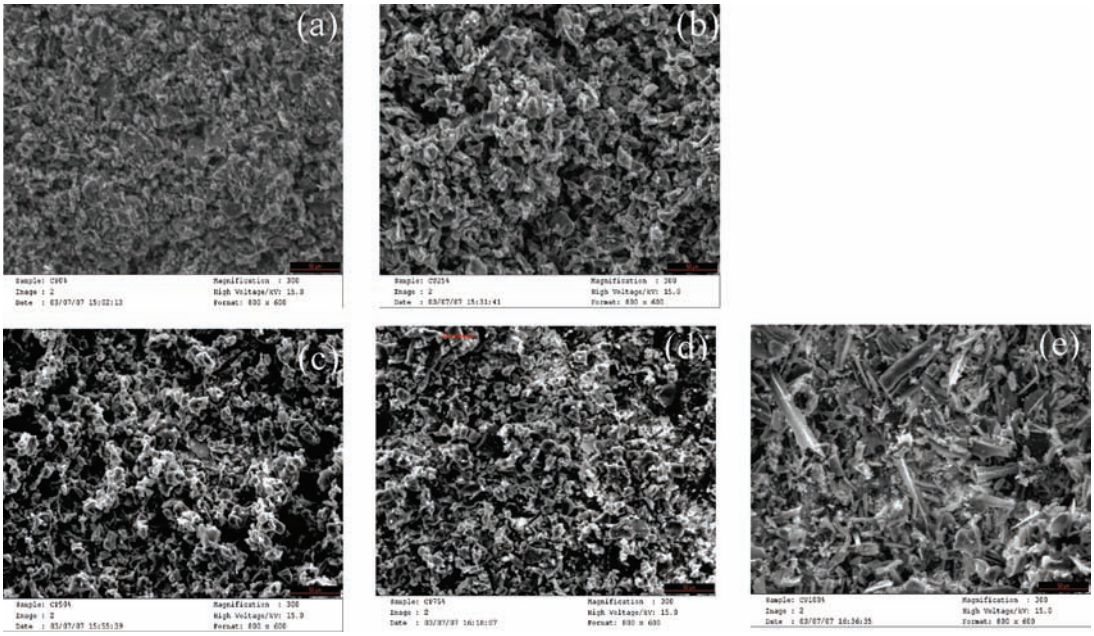

**Figure 4.** Scanning electron micrographs: (a) non-activated (0 %), (b) AC 25 %, (c) AC 50 %, (d) AC 75 %, and (e) AC 100 %.

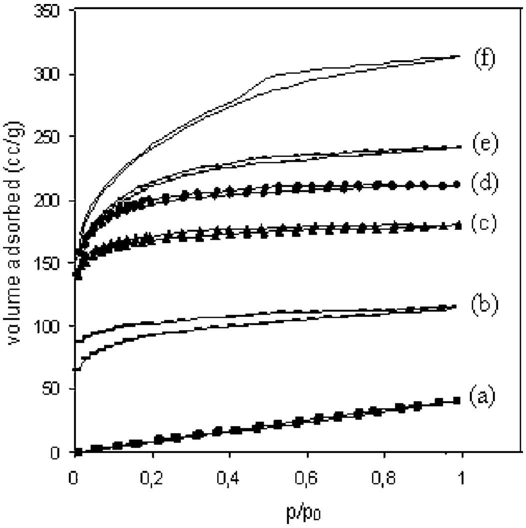

**Figure 5.** Adsorption and desorption isotherms of nitrogen for (a) coffee residue, (b) non-activated (0 %), (c) AC 25 %, (d) AC 50 %, (e) AC 75 %, and (f) AC 100 %.

dominant influences of the composition and structure of the precursors on their reactivity in the pyrolysis/activation reactions.

Boonamnuayvitaya et al.[14] have prepared carbon from coffee residue with an activation ratio equal to 75 % in the following experimental conditions: ambient temperature of 600 °C at a heating rate of 10 $°C \cdot min^{-1}$ under nitrogen gas flow for 4 h. They have obtained a mesoporous carbon with the following characteristics: $V_{tot} = 0.454\ cm^3 \cdot g^{-1}$; $V_{mic} = 0.090\ cm^3 \cdot g^{-1}$; $S_{BET} = 470\ m^2 \cdot g^{-1}$; $S_{mes} = 254\ m^2 \cdot g^{-1}$; and $d_p = 3.87$ nm. These characteristics are different than AC 75 % (Table 2). This dissimilarity can be attributed to the difference in the holding time, since a longer carbonization time enhances the porosity as was reported by Mohanty et al.[16] and to the difference in the used coffee residue physical properties which is displayed by the difference in the TGA results.

Nevertheless, a gradual spread of the two branches is observed from a $ZnCl_2$/MC activation rate equal to 50 % and to relative pressures greater than 0.4. This reveals a gradual development of the mesoporosity. This is very low for 50 % and 75 %, but much higher for the activated carbon 100 % since it presents a hysteresis loop type $H_2$ and, consequently, the existence of a significant amount of mesopores with no well-defined pore size and shape.[8]

Concerning the carbon prepared from the coffee residue without any $ZnCl_2$ impregnation (AC 0 %), it exhibits a hysteresis at low pressure. This type of hysteresis is associated with the expansion of distortions of the structure of carbon. Consequently, the molecules can pass through the narrow connections forming the porous network (low stiffness), but as these deformities are not perfectly elastic, they will form a trap for nitrogen, which will be released at low pressures.[17]

***3.4.2. Surface Area and Pore Volume.*** The values corresponding to the physical characteristics results from the $N_2$ adsorption−desorption isotherms of all analyzed carbons, such as total surface area ($S_{BET}$), the total porous volume ($V_{tot}$), the external surface area ($S_{ext}$), the microporous surface area ($S_{mic}$), the mesoporous surface area ($S_{mes}$), the microporous volume ($V_{mic}$), the mesoporous volume ($V_{mes}$), and the average pore diameter ($d_p$), are summarized in the Table 2.

Referring to the results in Table 2, one can see that the interval of microporosity presented by the analyzed solids ranges between (17.46 and 95.70) % since the lower value (17.46 %) corresponds to the coffee residue, and the non-activated carbon exhibits a microporosity of 75.14 %. The carbonization creates new micropores. The activation, with the different ratios, gives rise to more porosity. The maximum value (95.7 %) is attributed to the prepared carbon activated at 25 %.

Concerning the activated carbon, the mesoporosity increases with the increase of the activation ratio.

***3.4.3. Influence of the Activation Ratio on the Specific Surface Area and Pore Volume of Carbons Analyzed.*** The importance of the activation rate on the structure of the prepared carbons is illustrated in Figure 6. It indicates the influence of mass ratio of $ZnCl_2$/coffee residue on the surface represented by the specific surface area ($S_{BET}$), the surface of micropores ($S_{mic}$), and the surface of the mesopores (Figure 6a) on one hand, and on the other hand, the porous volume ($V_{tot}$), the microporous volume ($V_{mic}$), and the mesoporous volume ($V_{meso}$) are illustrated in Figure 6b.

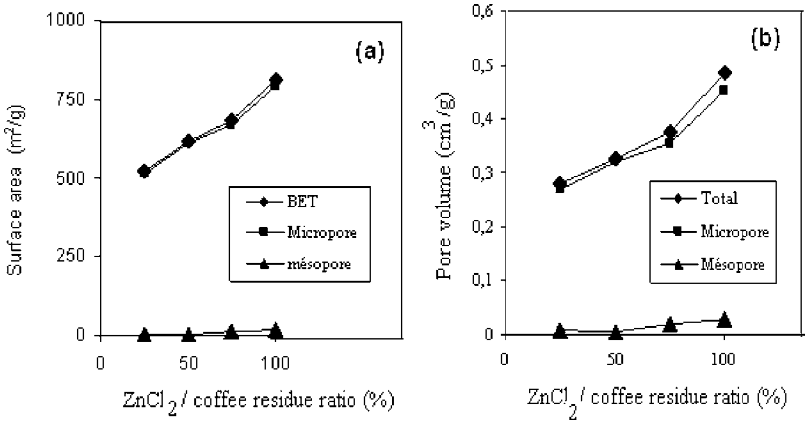

**Figure 6.** Influence of the activation ratio: (a) the specific surface areas and (b) the porous volumes.

**Table 2. Textural Characteristics of Carbons and Coffee Residue Determined from $N_2$ Adsorption Isotherms at 77 K**[a]

| carbon | $V_{tot}$ $cm^3 \cdot g^{-1}$ | $V_{mic}$ (DR) $cm^3 \cdot g^{-1}$ | microporosity ($V_{mic}/V_{0,99}$) % | $V_{mes}$ $cm^3 \cdot g^{-1}$ | $S_{BET}$ $m^2 \cdot g^{-1}$ | $S_{ext}$ $m^2 \cdot g^{-1}$ | $S_{mic}$ $m^2 \cdot g^{-1}$ | $d_p = 4\ V_{tot}/S_{BET}$ nm |
|---|---|---|---|---|---|---|---|---|
| non-activated (0 %) | 0.177 | 0.133 | 75.14 | 0.044 | 297.58 | 17.72 | 279.86 | 2.38 |
| AC 25 % | 0.279 | 0.267 | 95.70 | 0.012 | 519.70 | 140.93 | 378.77 | 2.15 |
| AC 50 % | 0.326 | 0.301 | 92.33 | 0.025 | 616.96 | 227.07 | 389.89 | 2.11 |
| AC 75 % | 0.374 | 0.305 | 81.55 | 0.069 | 680.35 | 359.41 | 391.84 | 2.20 |
| AC 100 % | 0.484 | 0.339 | 70.04 | 0.145 | 810.21 | 396.82 | 413.39 | 2.39 |

[a] $V_{tot}$: total volume; $V_{mic}$ (DR): microporous volume; $V_{meso}$: mesoporous volume; $S_{BET}$: BET surface; $S_{ext}$: nonmicroporous surface; $S_{mic}$: microporous surface; $d_p$: average pore diameter.

**Table 3. Salicylic Acid Adsorption Test onto Prepared Carbons ($C_i = 30\ mg \cdot L^{-1}$, $T = 25$ °C, pH 3, and 1 g of Carbon)**

| carbon | $q_e \pm \Delta q_e$ $mg \cdot g^{-1}$ | % removal | microporosity ($V_{mic}/V_{tot}$) % | acidic func/basic func |
|---|---|---|---|---|
| non-activated (0 %) | 19.72 ± 0.64 | 66.00 | 75.14 | 10.75 |
| AC 25 % | 29.03 ± 0.34 | 97.00 | 95.70 | 1.94 |
| AC 50 % | 28.05 ± 0.39 | 93.50 | 92.33 | 2.46 |
| AC 75 % | 28.38 ± 0.03 | 94.60 | 81.55 | 3.79 |
| AC 100 % | 28.62 ± 0.36 | 95.40 | 70.04 | 11.19 |

According to the Figure 6a, $S_{BET}$, $S_{mic}$, and $S_{mes}$ all increase simultaneously with an increase of the activation ratio. The increase in the mesoporous surface is lower compared to the $S_{BET}$ and $S_{mic}$.

The evolution of the pore volumes (total, microporous, and mesoporous) is similar to surface areas. They increase with an increase in the activation ratio.

The previous results confirm the influence of activation rate on the development of the porous structure of the activated carbon. This suggests that the presence of zinc chloride contributes not only to the creation of new micropores but also to the expansion of already existing pores in the structure. This result is in agreement with those of Rodríguez-Reinoso and Molina-Sabio[18] and Zhu et al.[19]

Depending on the conditions used, one of the two latter mechanisms could predominate, or both could take place at the same rate.

The results suggest that micropores are generated continuously and mesopores are formed by enlargement of micropores existing in parallel. Consequently, the two mechanisms occur simultaneously, with the domination of the micropore formation over mesopore development.

***3.5. Adsorption of Salicylic Acid.*** The efficiency of the prepared carbons has been tested by subjecting them to the adsorption of molecules of salicylic acid under the following conditions: $C_i = 30\ mg \cdot L^{-1}$, pH = 3 at room temperature ($T$ = 25 °C), and in the presence of 1 g of carbon. The results are reported in Table 3.

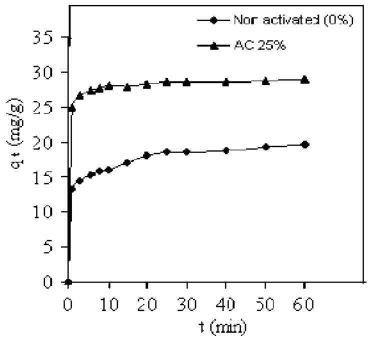

**Figure 7.** Adsorption kinetics for salicylic acid onto the non-activated carbon (0 %) and AC 25 % ($C_i = 30\ mg \cdot L^{-1}$, pH 3, and $T$ = 25 °C).

These values show that the activated carbon prepared with an activation ratio of 25 % is the most successful compared to the other carbons, which can be explained by the presence of a large microporosity (95.70 %) in addition to strong basicity of the surface (acidic function/basic function = 1.94). This result is in agreement with those of Koganovski et al. reported by Fierro et al.[20] who reported that the adsorption of phenolic compounds at low equilibrium concentrations on an activated carbon not only depends on the pore volume of the activated carbon but also on the ratio of the numbers of acidic to basic groups. The larger this ratio is, the lower the adsorption.

Figure 7 shows the effect of the activation process on the amount of salicylic acid adsorbed ($mg \cdot g^{-1}$) at different contact times. The amount of salicylic acid uptake $q_t$ ($mg \cdot g^{-1}$) increased with an increase in agitation time, and the adsorption process reached equilibrium at around (10 and 25) min for AC 25 % and non-activated carbon (0 %), respectively. We can notice that the uptake was faster and the amount of salicylic adsorbed was more important when the absorbent used was AC 25 %. Moreover, the amount of salicylic acid uptake increased with the activation process.

## 4. Conclusion

The coffee residue can be efficiently recovered and converted into a carbon chemically activated with $ZnCl_2$. The latter acts as both a dehydration and an activation agent. It has been shown that the mass ratio (mass of $ZnCl_2$/mass of coffee residue), called the activation ratio, affects the physicochemical properties of the prepared carbon. Therefore, it is possible through a judicious choice of the activation ratio to obtain an activated carbon with desired characteristics.

The adsorption tests of salicylic acid by the prepared carbons showed that the performance of the process depends on the activation ratio, and 25 % $ZnCl_2$ appears to be the most effective for the adsorption of salicylic acid in the indicated conditions.

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