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The Influence of NH$_4$NO$_3$ and NH$_4$ClO$_4$ on Porous Structure Development of Activated Carbons Produced from Furfuryl Alcohol

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Abstract: The influence of NH$_4$NO$_3$ and NH$_4$ClO$_4$ on the porous texture and structure development of activated carbons produced from a non-porous polymeric precursor synthesized from furfuryl alcohol has been studied. The non-doped counterparts were prepared and studied for comparison purposes. NH$_4$NO$_3$ and NH$_4$ClO$_4$-doped polymers were carbonized under N$_2$ atmosphere at 600 °C, followed by CO$_2$ activation at 1000 °C and the obtained carbon materials and activated carbons were thoroughly characterized. The porosity characterization data have shown that NH$_4$NO$_3$-derived ACs present the highest specific surface area (up to 1523 m$^2$/g) in the experimental conditions studied, and the resulting porosity distributions are strongly dependent on the activation conditions. Thus, 1 h activation is optimum for the microporosity development, whereas larger activation times lead to micropores enlargement and conversion into mesopores. The type of doping salts used also has a substantial impact on the surface chemical composition, i.e., C=O groups. Moreover, NH$_4$NO$_3$ and NH$_4$ClO$_4$ constitute good sources of nitrogen. The type and contribution of nitrogen species are dependent on the preparation conditions. Quaternary nitrogen only appears in doped samples prepared by carbonization and pyrrolic, pyridinic, and nitrogen oxide groups appear in the NH$_4$NO$_3$-series. NH$_4$NO$_3$ incorporation has led to optimized materials towards CO$_2$ and C$_2$H$_4$ sorption with just 1 h activation time.

Keywords: activated carbons; carbonaceous materials; pore development; CO$_2$ adsorption; CO$_2$ uptake; supercapacitors; ethylene adsorption; furfuryl alcohol; hydrogen storage; methylene blue adsorption

1. Introduction

For several years, the main topic of researchers in activated carbons (ACs) has been developing porosity, which is one of the most important features of this type of material. The final porosity developed is often dependent on the used precursor. For the most part, activated carbons are produced from biomass like wood [1,2], stems [3], peels of fruits [4–6], or leaves [7]. Pores, which derive from the natural vascular system in this type of biomass precursors, are further developed in activated carbons obtained from them [8]. The second group of precursors is polymers, which are characterized by a non-porous structure and do not contain any impurities, such as silica or metal oxides, in their chemical composition [9,10]. Comparing these two kinds of precursors, it is claimed that biomass-derived activated carbons will have a more developed porous structure than polymer-derived carbonaceous materials because of the contained original pores in the former. Also, the less ordered structure of biomass precursors in comparison with polymeric ones explains that larger porosity usually developed in the former under comparable activation conditions [11]. However, in contrast to polymer precursors, biomass counterparts contain...
mineral matter, which could act as a catalyst and accelerate the decomposition of the precursor during pyrolysis [12,13]. Additionally, the ashes derived from mineral matter could block pores and interfere with the adsorption processes [14,15]. Moreover, the presence of ash in carbonaceous materials can constitute a disadvantage in their different applications, e.g., in the production of carbon electrodes. Therefore, the choice of an appropriate precursor, with pure chemical composition and highly developed porous structure, could pose an issue. One solution to this problem is using furfuryl alcohol as a precursor in ACs production. Furfuryl alcohol is produced from biomass via its dehydration followed by catalytic hydrogenation of furfural [16–19]. A highly pure chemical composition is the result of repeated distillation/extraction processes. To sum up, it constitutes a promising precursor to activated carbons with high porosity and pure chemical composition. Moreover, using this type of precursor ash removal processes prior to activation could be omitted. This allows for the reduction of production costs and consumption of chemical reagents (i.e., HCl or distilled water) [20,21].

Currently, methods of porous texture development are divided into two groups: physical and the so-called chemical activation [22–28]. Physical activation is usually conducted under CO$_2$ or steam atmosphere at a temperature ranging from 800 °C to 1000 °C [29–31]. Rodriguez-Reinoso and co-workers reported that CO$_2$ activation leads to narrow micropores creation and, subsequently, their widening occurs [32]. In the case of steam, the widening of pores occurs from the early stages of activation. Apart from the conventional method of heating, porosity could be developed through unconventional heating methods, such as microwave or plasma treatment. In comparison to conventional heating, microwave heating is conducted under milder conditions such as lower temperatures, shorter processing times, and requires less energy [33,34]. Additionally, this method implies fewer requirements for feedstock pre-treatment. The main difference between conventional and microwave heating lies in their mechanism. In the case of conventional heating, a particle is heated from the external surface to the core, whereas in microwave heating, a particle is heated from the core to the external surface. The second unconventional method of pores creation is plasma treatment. Plasma could be created from the following gases: oxygen, nitrogen, argon, ammonia, or air [35–37]. In this method, the surface of the sample is bombarded with ions or free radicals. It leads to the breaking of sp$^2$ bonds in the carbon structure and the introduction of functional groups, which promote carbon etching. Inaccessible pores are opened and pore walls are collapsed. It causes an increase in porosity. Some advantages of plasma treatment include that it is faster than conventional heating and does not require solvents or toxic chemicals, being also highly efficient compared to chemical activation [35].

In the case of chemical activation methods, they are based on using mainly KOH, NaOH, K$_2$CO$_3$, H$_3$PO$_4$, or less frequently ZnCl$_2$ [6,34,38–53]. Additionally, in carbonaceous materials preparation, some researchers used the following chemical compounds: FeCl$_2$, NaCl, KCl, Fe$_2$(SO$_4$)$_3$, (Na[Al(OH)$_4$]), or Na$_2$SiO$_3$ [54,55]. Recently, researchers are also paying attention to the influence of ammonium nitrate (NH$_4$NO$_3$) on porosity development. Subramanian and Viswanathan prepared activated carbon from sucrose and ammonium nitrate by carbonization in the temperature range from 600 °C to 900 °C [56]. They reported that activation with ammonium nitrate caused an increase in porosity. Apart from that, they checked the impact of the sucrose/ammonium nitrate mass ratio on pores development. Based on TGA-DTG analysis, they noted that the addition of ammonium nitrate increases the stability of the sample. The highest mass loss was observed at 438–448 °C. Bayrak et al. produced carbonaceous materials from rice husks for Cr$^{6+}$, Cu$^{2+}$, and Ni$^{2+}$ removal from water [57]. In their study, they used the following compounds as activating agents: NH$_4$Cl, NH$_4$Br, NH$_4$I, (NH$_4$)$_2$HPO$_4$, NH$_4$HCO$_3$ and NH$_4$NO$_3$. Comparing the mentioned compounds, ammonium nitrate caused the highest development of the porous structure. In contrast, the lowest impact on porosity was shown by ammonium iodide. Additionally, they noted that mesopores prevailed in activated carbons obtained by ammonium salts activation. Zheng and co-workers produced nitrogen/sulfur co-doped carbonaceous materials
for supercapacitors application [7]. In their study, they utilized ginkgo leaves as precursors and examined the influence of ammonium nitrate on porous structure development. Additionally, they described the decomposition of ammonium nitrate, which takes place at temperatures over 220 °C. The authors claimed that activation is a redox reaction, and as a result of the increase of the heat-treatment temperature, ammonium nitrate is melted and partially decomposed to HNO$_3$(g), NH$_3$(g), N$_2$O, and H$_2$O(g). Simultaneously, the oxidation reaction of biomass-derived carbon takes place. Gaseous products, such as CO$_2$, H$_2$O, NO$_2$, and N$_2$O, swell in graphene sheet-like carbon and further promote porous structure creation. In Table 1, specific surface areas of activated carbons obtained by ammonium nitrate activation are compiled.

As shown in the table above, all the activated carbons were prepared via chemical activation of biomass, in which original pores exist. Based on the literature, among the utilized chemical compounds containing NH$_4^+$, the ammonium nitrate ion has the highest impact on pores development. To the best of our knowledge, there are no scientific reports about ammonium perchlorate (NH$_4$ClO$_4$), which is also a strong oxidant. In industry, NH$_4$ClO$_4$ is commonly utilized as a solid rocket propellant. NH$_4$ClO$_4$ starts to decompose at 130 °C, and the main decomposition products include steam, nitrogen, oxygen, and chlorine [60,61]. From an environmental point of view, the produced chlorine leads to ozone layer degradation. For this reason, the produced chlorine should be adsorbed and utilized in other processes, such as in water disinfection tasks [62].

Taking all this into account, the general objectives of this study are to compare and examine the influence of ammonium nitrate and ammonium perchlorate on the preparation of activated carbon, paying attention to properties such as pore volume and distribution, specific surface area, size of crystallites and chemical composition. These carbonaceous materials will be prepared from furfuryl alcohol. Therefore, the impact of any silica and metal oxides, present in other precursors, on pore creation will be eliminated. The potential application of the obtained materials will be the adsorption of gases. Therefore, carbon dioxide (CO$_2$) and ethylene (C$_2$H$_4$) will be used as model gases. Both gases negatively affect the environment. CO$_2$ is one of the greenhouse gases whose emission is still increasing [63]. Currently, the concentration of CO$_2$ in the atmosphere is 415 ppm. It mainly comes from anthropogenic sources, such as fossil fuel combustion or cement production. The high concentration of CO$_2$ intensifies the greenhouse effect, which results in various climatic disasters, for example, droughts, melting of glaciers, and forest fires. C$_2$H$_4$ is known to be a plant hormone, which controls the ripening processes [64]. It is produced during the putrefactive processes of plants and leads to the faster ripening of vegetables that are nearby. For this reason, the regulation of the concentration of C$_2$H$_4$ is especially important in the case of vegetable and fruit storage in the food industry. Note that these selected

| Sample       | Preparation Parameters                                                                 | Specific Surface Area [m$^2$/g] | Ref. |
|--------------|----------------------------------------------------------------------------------------|----------------------------------|------|
| C$_{NA900}$  | Sucrose/NH$_4$NO$_3$ mass ratio 3:1 (C$_{NA900}$) and 2:1 (C$_{NB900}$). Carbonization under N$_2$ atmosphere for 6 h at 900 °C. | 489                              | [56] |
| C$_{NB900}$  |                                                                                       | 518                              |      |
| AC$_{NH4NO3}$| Rice husk/NH$_4$NO$_3$ mass ratio: 1:4. Carbonization under N$_2$ atmosphere for 0.5 h at 600 °C. | 457                              | [57] |
| AN/GL$_{700}$| Ginkgo leaves/NH$_4$NO$_3$ mass ratio: 1:2. Carbonization under N$_2$ atmosphere for 1 h at 700 °C. | 672                              | [7]  |
| PWAC         | Pistachio wood wastes/NH$_4$NO$_3$ impregnation ratio: 5% wt. Pyrolysis under N$_2$ atmosphere at 800 °C for 2 h. | 1448                             | [58] |
| N-carbon$_{700}$ | Cellulose/NH$_4$NO$_3$/distilled water mass ratio 1:1:10. Hydrothermal carbonization at 240 °C for 5 h. Activation with KOH at 700 °C and 800 °C for 1 h. | 1184                             | [59] |
| N-carbon$_{800}$ |                                                                                      | 1976                             |      |
molecules differ in their kinetic diameters. They are 0.33 nm and 0.39 nm for CO₂ and C₂H₄, respectively.

2. Materials and Methods

2.1. Materials

In this study, the preparation scheme can be summarized as follows: either a mixture of furfuryl alcohol, maleic acid, and ethylene glycol (Mixture 1) or a mixture of furfuryl alcohol, maleic acid, and ethylene glycol with either NH₄NO₃ or NH₄ClO₄ (Mixture 2) led to polymeric materials, that were carbonized in a nitrogen atmosphere at 600 °C. The derived materials were characterized as obtained, and also after their activation with CO₂ at 1000 °C for different holding times.

The samples obtained after carbonization were named AC in the Mixture 1 scheme, or either AC_NH₄NO₃ or AC_NH₄ClO₄ in the Mixture 2 carbonization scheme. Note that in the case of Mixture 2, this “carbonization” can really imply some chemical activation as well. Additionally, these materials were submitted to activation by CO₂. In this case, their nomenclature includes a number representing the holding time of the CO₂ activation step (in hours). A detailed description of the preparation scheme is shown next.

An activation precursor was prepared from 15 mL furfuryl alcohol (Nr. CAS: 98-00-0, Sigma Aldrich), 2 g maleic acid (Nr. CAS: 110-16-7, Chempur), and 14 mL ethylene glycol (Nr. CAS: 107-21-1, EUROCHEM). All reagents were mixed on the magnetic stirrer for 30 min at ambient temperature. Afterward, the mixture was heated in an oven from 40 °C to 200 °C. It was held for 10 min at 40 °C, 50 °C, 80 °C, and for 18 h at 200 °C. After heating, the obtained polymeric precursor was cooled at an ambient temperature and ground.

In the case of chemically activated materials, NH₄NO₃ (Nr. CAS: 6484-52-2, Chempur) or NH₄ClO₄ (prepared from ammonia water (Nr. CAS: 1336-21-6, STANLAB) and perchloric acid (Nr. CAS: 7601-90-3, Chempur)) salts were firstly dissolved in 14 mL ethylene glycol. An amount of 1 g NH₄NO₃ or 1 g NH₄ClO₄ was added. After that, the solutions were added to the furfuryl alcohol and maleic acid mixture (same quantities as in the previous conditions). All reagents were mixed on the magnetic stirrer for 30 min at an ambient temperature. Afterward, the mixture was heated in an oven from 40 °C to 200 °C. It was held for 10 min at 40 °C, 50 °C, 80 °C, and for 18 h at 200 °C. After heating, each obtained precursor polymer was cooled at an ambient temperature and ground.

The three different precursors (either prepared with NH₄NO₃, NH₄ClO₄, or without any of those) were subjected to a carbonization process under N₂ atmosphere at 600 °C (temperature ramp 5 °C/min) for 4 h in an electric tube furnace (STF 15/180, Carbolite Gero). The flow of N₂ was 100 mL/min. The three obtained materials were characterized as obtained and also submitted to a next step. In it, 1 g of each resulting sample was activated under CO₂ atmosphere at 1000 °C (temperature ramp 5 °C/min) for 1 h, 2 h, or 3 h. The flow of CO₂ was 50 mL/min during the whole process.

For simplicity, in some parts of the discussion these three sets of samples are referred to as “unmodified”, “NH₄NO₃ modified”, or “NH₄ClO₄ modified”.

The purity of N₂ and CO₂ were 5.0 and 4.5, respectively. Both gases were provided by Messer.

2.2. Methods

The porous structure of the obtained activated carbons was characterized using volumetric analysis (Autosorb, Quantachrome; Boynton Beach, USA). Pore volume and pore size distribution were determined based on N₂ adsorption/desorption isotherms at −196 °C using the QSDFT model. Specific surface areas were calculated from the BET equation applied to the N₂ adsorption data. Additionally, adsorption of CO₂ at 0 °C allowed to determine the pores with diameters lower than 1.0 nm. In this case, the pore size distribution was determined using the NLDFT model. The porosity characterization data were calculated using QuadraWin software.
The structural properties of the ACs were analyzed using X-ray powder diffraction (Empyrean, PANalytical; Malvern, UK). Measurements were conducted in the $5^\circ$–$80^\circ$ range using copper radiation ($K_c=0.154056$ nm). HighScore Plus software was used for XRD patterns interpretation and for stacking height ($L_c$) and lateral size ($L_a$) calculation.

Disorder degrees in the ACs were estimated using Raman spectroscopy analysis (Jasco NRS-5100; Easton, USA). Measurements were carried out with an Ar laser (wavelength = 532.11 nm, power = 2.0 mW, magnification of the objective = 20x). The activated carbons were scanned from 70 cm$^{-1}$ to 3780 cm$^{-1}$.

X-ray photoelectron spectroscopy was used to confirm the surface chemical composition of the carbons (PREVAC; Rogów, Poland). Functional groups were determined based on C 1s, O 1s, and N 1s signals. Data were calculated using CasaXPS 2.3.16 software.

Thermal stabilities of the carbonaceous materials were determined using a thermobalance (NETZSCH, STA 449F5; Selb, Germany). An amount of 10 mg of sample was heated from 50 °C to 950 °C with a temperature ramp of 20 °C/min. Measurements were conducted both under an argon or oxygen atmosphere. The flow of gases was 30 mL/min or 50 mL/min, respectively.

To test the ACs in their final application, adsorption measurements of CO$_2$ and C$_2$H$_4$ were conducted under an argon atmosphere. The flow of CO$_2$ and C$_2$H$_4$ was 30 mL/min or 50 mL/min, respectively.

To test the ACs in their final application, adsorption measurements of CO$_2$ and C$_2$H$_4$ were conducted on a homemade thermobalance operating under 1025 hPa. Firstly, 0.4 g of AC sample was heated to 250 °C to remove adsorbed compounds and moisture. The sample was held for 10 min at this temperature. After that, it was cooled to 30 °C under the investigated gas atmosphere. The flow of CO$_2$ and C$_2$H$_4$ was 40 mL/min. Sorption capacities were calculated based on the mass difference between 250 °C and 30 °C.

3. Results and Discussion

3.1. Porous Structure

3.1.1. N$_2$ Adsorption at −196 °C

N$_2$ adsorption/desorption isotherms are presented in Figure 1.

![N$_2$ Adsorption Isotherms](image.png)

**Figure 1.** N$_2$ adsorption/desorption isotherms at −196 °C of samples: (a) AC series, (b) NH$_4$NO$_3$ series, and (c) NH$_4$ClO$_4$ series.

Figure 1 shows that the carbonization of the three different precursors leads to a very similar and poor porosity. Hence, the discussion is focused on data from samples after CO$_2$ activation. According with the IUPAC classification, the obtained isotherms (Figure 1) are type I (b) [65]. They are characteristic of materials having wide micropores and narrow mesopores (<~2.5 nm). In this case, N$_2$ adsorption is enhanced in the NH$_4$ClO$_4$ series and, especially, in the NH$_4$NO$_3$ series: comparing the influence of NH$_4$NO$_3$ and NH$_4$ClO$_4$ on N$_2$ adsorption it can be seen that higher N$_2$ adsorption was achieved in the NH$_4$NO$_3$-derived carbons.

Focusing on NH$_4$NO$_3$, larger N$_2$ adsorption was observed in AC-NH$_4$NO$_3$-2h in comparison to sample AC-NH$_4$NO$_3$-3h, and also their porosity distributions were noticeably
different. This was not observed in the AC and NH₄ClO₄-modified samples (carbonized in N₂ and activated with CO₂). The comparison between these two series highlights that the activation reaction in the NH₄NO₃ series proceeds in a much more efficient way than in the NH₄ClO₄ one. From a certain activation time (i.e., 3 h), a noticeable porosity widening is noticed in the NH₄NO₃ series, and even some porosity destruction, so the selection of the activation time is very important. The impact of activating salts on pore size distributions is presented in Figure 2.

![Figure 2](image_url)

**Figure 2.** Pore size distribution of samples (a) AC series, (b) NH₄NO₃ series, (c) NH₄ClO₄ series calculated from N₂ adsorption data at −196 °C.

This figure confirms that differences in the pore size distributions are noted for the three series of samples and, in general, the larger activation times lead to larger porosities. In the ACs series, the highest porosity was reached in the sample AC_3h, whose mean pore size is around 2.0 nm. The mean pore size for NH₄ClO₄_3h is around 2.5 nm, whereas it reaches 3.0 nm for NH₄NO₃_3h.

Although higher pore volumes are in general present in the NH₄NO₃ series in comparison with the NH₄ClO₄ one, these differences minimize for 3 h activation time.

In Table 2, specific surface areas and pore volumes calculated from N₂ adsorption data are presented.

| Sample          | SSA ¹ [m²/g] | V_total [cm³/g] | V_micro ² [cm³/g] | V_meso ³ [cm³/g] |
|-----------------|--------------|-----------------|-------------------|------------------|
| AC              | 28           | 0.03            | 0.00              | 0.03             |
| AC_1h           | 535          | 0.22            | 0.19              | 0.01             |
| AC_2h           | 843          | 0.36            | 0.30              | 0.03             |
| AC_3h           | 1174         | 0.55            | 0.36              | 0.15             |
| AC_NH₄NO₃      | 57           | 0.04            | 0.02              | 0.02             |
| AC_NH₄NO₃_1h    | 999          | 0.43            | 0.34              | 0.04             |
| AC_NH₄NO₃_2h    | 1523         | 0.75            | 0.41              | 0.28             |
| AC_NH₄NO₃_3h    | 1292         | 0.71            | 0.26              | 0.39             |
| AC_NH₄ClO₄     | 6            | 0.01            | 0.00              | 0.00             |
| AC_NH₄ClO₄_1h   | 696          | 0.28            | 0.24              | 0.02             |
| AC_NH₄ClO₄_2h   | 933          | 0.40            | 0.27              | 0.09             |
| AC_NH₄ClO₄_3h   | 1342         | 0.62            | 0.29              | 0.26             |

¹ SSA—The specific surface area, calculated by the BET equation. ² V_micro—The volume of pores with diameter lower than 2 nm, determined from N₂ adsorption. ³ V_meso—The volume of pores with diameter in the range from 2 nm to 50 nm, estimated from N₂ adsorption.
This table shows that carbons obtained only through the “carbonization” process in N$_2$ at 600 °C are characterized by low specific surface areas. In the case of AC, this sample is indeed obtained by carbonization. In AC$_{NH_4NO_3}$ and AC$_{NH_4ClO_4}$, some chemical activation may occur as well (due to the chemical compounds incorporated during the preparation of the precursor). This is especially remarkable in the AC$_{NH_4NO_3}$ sample, and explains the 57 m$^2$/g of surface area reached.

The porosity values in AC$_{NH_4NO_3}$ and AC$_{NH_4ClO_4}$ series are lower than, for example, those reported by Bayrak and co-workers, who used rice husks as precursors [57]. Although the activation temperature is the same in both cases, the higher specific surface areas reported by Bayrak et al. may be very much influenced by the different nature of the precursor.

Sample AC$_{NH_4NO_3_2h}$ reached the highest BET specific surface area (1523 m$^2$/g) and the highest volume of micropores (0.41 cm$^3$/g). After the extension of the activation time to 3 h, the volume of micropores decreased by half and the mesopore volume increased. In the case of the NH$_4$ClO$_4$ series, the highest specific surface area and pores volume was exhibited by sample AC$_{NH_4ClO_4_3h}$ (1342 m$^2$/g and 0.29 cm$^3$/g, respectively). Comparing the effect of NH$_4$NO$_3$ and NH$_4$ClO$_4$, it has been found that NH$_4$NO$_3$ is more efficient for porosity development.

It is difficult to compare the ACs produced in the present study with those from other papers. For example, Mu et al. produced activated carbons by hydrothermal method followed by KOH activation at 800 °C for 1 h [59]. The highest specific surface area reached was 1976 m$^2$/g. It must be noted that so-developed porous structure is partially related to using KOH, one of the most effective activating agents, but also the proportion of chemical agent needs to be taken into consideration.

### 3.1.2. CO$_2$ Adsorption at 0 °C

Figure 3 presents the CO$_2$ adsorption/desorption isotherms at 0 °C for the different samples, which shows, that in general, CO$_2$ adsorption is lowest for the carbonized samples, whereas those activated for 1 h activation show the highest CO$_2$ adsorption. Increasing the activation time beyond 1 h leads to a decrease in the narrow micropores (characterized by CO$_2$ adsorption), being such a decrease is especially remarkable for NH$_4$NO$_3$$_3h$. The similarity in the AC and NH$_4$ClO$_4$ series remarks that no benefit, from the point of view of narrow micropore development, occurs by incorporating this chemical agent into the composition of the precursor, and only NH$_4$NO$_3$$_1h$ is interesting from that point of view.

![Figure 3](image-url)  
**Figure 3.** CO$_2$ adsorption/desorption isotherms at 0 °C for (a) AC series, (b) NH$_4$NO$_3$ series, (c) NH$_4$ClO$_4$ series.

Figure 4 highlights that from the point of view of the CO$_2$ pore size distributions, there are no important differences between the series. More remarkably, in the just-carbonized carbons, there is an increase in the volume of pores in the diameter range from 0.3 nm to 0.7
for AC\textsubscript{NH\textsubscript{4}NO\textsubscript{3}} and AC\textsubscript{NH\textsubscript{4}ClO\textsubscript{4}}. After activation, micropore size distributions were comparable for all the obtained samples and the differences between them were negligible.

Figure 3. CO\textsubscript{2} adsorption/desorption isotherms at 0 °C for (a) AC series, (b) NH\textsubscript{4}NO\textsubscript{3} series, (c) NH\textsubscript{4}ClO\textsubscript{4} series.

Figure 4 highlights that from the point of view of the CO\textsubscript{2} pore size distributions, there are no important differences between the series. More remarkably, in the just-carbonized carbons, there is an increase in the volume of pores in the diameter range from 0.3 nm to 0.7 nm for AC\textsubscript{NH\textsubscript{4}NO\textsubscript{3}} and AC\textsubscript{NH\textsubscript{4}ClO\textsubscript{4}}. After activation, micropore size distributions were comparable for all the obtained samples and the differences between them were negligible.

![Graph showing micropore size distributions for various samples](image)

Table 3. CO\textsubscript{2} micropore specific surface areas and micropore volumes for the prepared ACs.

| Sample      | CO\textsubscript{2} Micropore Specific Surface Area \(^1\) [m\textsuperscript{2}/g] | V\textsubscript{total} [cm\textsuperscript{3}/g] | V\textsubscript{0.7 nm} \(^2\) [cm\textsuperscript{3}/g] | V\textsubscript{0.8 nm} \(^3\) [cm\textsuperscript{3}/g] | V\textsubscript{1.0 nm} \(^4\) [cm\textsuperscript{3}/g] |
|-------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| AC          | 454                             | 0.15            | 0.10            | 0.10            | 0.12            |
| AC\_1h      | 706                             | 0.27            | 0.15            | 0.16            | 0.21            |
| AC\_2h      | 686                             | 0.27            | 0.14            | 0.16            | 0.21            |
| AC\_3h      | 589                             | 0.25            | 0.12            | 0.14            | 0.19            |
| AC\textsubscript{NH\textsubscript{4}NO\textsubscript{3}} | 496                             | 0.16            | 0.11            | 0.11            | 0.13            |
| AC\textsubscript{NH\textsubscript{4}NO\textsubscript{3}}\_1h | 724                             | 0.29            | 0.15            | 0.17            | 0.22            |
| AC\textsubscript{NH\textsubscript{4}NO\textsubscript{3}}\_2h | 640                             | 0.27            | 0.13            | 0.15            | 0.21            |
| AC\textsubscript{NH\textsubscript{4}NO\textsubscript{3}}\_3h | 435                             | 0.19            | 0.09            | 0.10            | 0.14            |
| AC\textsubscript{NH\textsubscript{4}ClO\textsubscript{4}} | 471                             | 0.15            | 0.10            | 0.10            | 0.13            |
| AC\textsubscript{NH\textsubscript{4}ClO\textsubscript{4}}\_1h | 651                             | 0.25            | 0.14            | 0.15            | 0.19            |
| AC\textsubscript{NH\textsubscript{4}ClO\textsubscript{4}}\_2h | 600                             | 0.25            | 0.13            | 0.14            | 0.19            |
| AC\textsubscript{NH\textsubscript{4}ClO\textsubscript{4}}\_3h | 587                             | 0.27            | 0.11            | 0.13            | 0.20            |

\(^1\) SSA\textsubscript{CO2}—The micropore specific surface area obtained on the basis on CO\textsubscript{2} adsorption at 0 °C. \(^2\) V\textsubscript{0.7 nm}—The volume of pores with diameter up to 0.7 nm, determined from CO\textsubscript{2} adsorption. \(^3\) V\textsubscript{0.8 nm}—The volume of pores with diameter up to 0.8 nm, determined from CO\textsubscript{2} adsorption. \(^4\) V\textsubscript{1.0 nm}—The volume of pores with diameter up to 1.0 nm, determined from CO\textsubscript{2} adsorption.
Table 3 confirms that the addition of oxidizing salts to the composition of the precursors caused insignificant changes in the narrow microporous structure: comparing the AC, NH₄NO₃ and NH₄ClO₄ series, noticeable differences were not observed. The highest microporous specific surface area and micropores volume were exhibited by the sample AC_NH₄NO₃_1h. They were 724 m²/g and 0.29 cm³/g, respectively.

3.2. Structural Properties
3.2.1. X-ray Diffraction Analysis

XRD patterns for all obtained activated carbons are presented in Figure 5. They present two main reflections at positions 24° and 45°. Their Miller indexes are (002) and (10), respectively [66].

In the case of just-carbonized carbons, peaks for (002) reflection, which corresponds to the spacing between graphenic planes, are high and wide. Activation processes lead to their intensity decreasing and peak narrowing with the extension of the activation time. A more pronounced (002) reflection decrease (i.e., for 3 h activation time with respect to the carbonized sample) is observed in the NH₄NO₃ series in comparison to AC and NH₄ClO₄ ones.

For all the obtained just-carbonized samples, (10) reflections are broad and smooth. The position of (10) reflections is changing with the lateral size of carbon pieces. This feature, and the origin of (10) reflection are very well described in detail elsewhere [66,67].

1 h activation processes led to the increase of the intensity of peaks corresponding to those reflections, becoming narrower and sharper. Moreover, the extension of the activation time caused a slight decrease in the intensity of the peaks associated to the (10) reflections.

Based on obtained XRD patterns, stacking height (Lc) and lateral size (La) of carbon crystallites were calculated from the following equations:

\[ Lc = \frac{0.89 \lambda}{Bc \cos \theta_c} \]  \hspace{1cm} (1)

\[ La = \frac{1.89 \lambda}{Ba \cos \theta_a} \]  \hspace{1cm} (2)

where \( \theta \) is the angle of a reflection, \( \lambda \) is wavelength of X-rays, and \( Bc \) and \( Ba \) are full widths at half maximum (FWHM) of (002) and (10) reflections, respectively.

Stacking height (Lc), lateral size (La) and interlayer distance (d₀₀₂) of carbon crystallites are presented in Table 4.
Table 4. Stacking height (Lc), lateral size (La) and interlayer distance (d_{002}) of carbon crystallites.

| Sample            | Lc [nm] | La [nm] | d_{002} [nm] |
|-------------------|---------|---------|--------------|
| AC                | 1.0     | 1.9     | 0.381        |
| AC_1h             | 0.9     | 3.1     | 0.392        |
| AC_2h             | 1.1     | 3.2     | 0.387        |
| AC_3h             | 0.9     | 3.2     | 0.388        |
| AC_NH_4NO_3       | 0.9     | 1.9     | 0.394        |
| AC_NH_4NO_3_1h    | 1.1     | 3.1     | 0.381        |
| AC_NH_4NO_3_2h    | 1.2     | 3.3     | 0.373        |
| AC_NH_4NO_3_3h    | 1.2     | 3.5     | 0.371        |
| AC_NH_4ClO_4      | 0.7     | 1.9     | 0.417        |
| AC_NH_4ClO_4_1h   | 1.0     | 3.1     | 0.388        |
| AC_NH_4ClO_4_2h   | 1.0     | 3.3     | 0.387        |
| AC_NH_4ClO_4_3h   | 1.1     | 3.3     | 0.384        |

These data show that modification of the parent polymers with the NH₄NO₃ or NH₄ClO₄ salts caused substantial changes in the stacking height of carbon crystallites during the carbonization process, whereas the lateral size was not affected. In comparison with AC, AC_NH₄ClO₄ shows a decrease in stacking height from 1.0 nm to 0.7 nm. In the case of AC_NH₄NO₃, this difference was only 0.1 nm.

After the activation processes, the lateral size significantly increased, whereas the stacking height increased only slightly. Sample AC_NH₄NO₃_3h exhibited the highest value of Lc and La. They were 1.2 nm and 3.5 nm, respectively. The same material presented the highest volume of mesopores (0.39 cm³/g). In the case of sample AC_NH₄NO₃_2h, which has the highest specific surface area, Lc and La values are 1.2 nm and 3.3 nm, respectively. Therefore, an increase of lateral size could also be related to the development of porosity.

3.2.2. Raman Spectroscopy

The ordered and defective carbon structures in the carbonaceous materials were estimated on the basis of the intensity ratio of D-band to G-band (I_D/I_G). The formation of the D-band appears near 1345 cm⁻¹ and is related to disordered structure. On the other hand, the G-band is associated with the regular structure of carbon and appears near 1596 cm⁻¹. The crystallites size (La) [68–70] were determined based on the following equation, and are compiled in Table 5:

\[
La = \frac{C}{R}
\]

where R is the I_D/I_G intensity ratio of D-band to G-band and constant C is 35 in this study.

The carbonized samples prepared with the doped polymers show a higher disordered structure than the one prepared with the undoped polymer. Comparing the influence of the type of salts, it can be noted that carbons from the NH₄NO₃ series are characterized by a more disordered structure than those from NH₄ClO₄ series. After the activation processes, the disordered structure significantly increased. The highest increase in I_D/I_G ratio was exhibited after 3 h activation by all the obtained samples. The I_D/I_G ratio for them was 1.09.

The largest size of crystallites (La) was exhibited by the sample AC. It was 5.9 nm. Significantly lower La values were exhibited by the carbonized samples from NH₄NO₃ and NH₄ClO₄ series. They were 4.9 nm and 5.1 nm, respectively. Further activation processes caused a decrease in the size of carbon crystallites. Moreover, this results in similar sizes of crystallites. The lowest carbon crystallites were exhibited by all the samples after 3 h activation.

The structural parameters La obtained by Raman are in good agreement with La determined by the XRD method.
Table 5. \( I_D/ I_G \) ratios and carbon crystallites (La) size of obtained activated carbons.

| Sample           | \( I_D/ I_G \) Ratio | D-Band Width [cm\(^{-1}\)] | G-Band Width [cm\(^{-1}\)] | La [nm] |
|------------------|-----------------------|-----------------------------|----------------------------|---------|
| AC               | 0.60                  | 272.81                      | 77.48                      | 5.9     |
| AC\(_{NH}_4\)NO\(_3\) | 0.71                  | 283.99                      | 85.86                      | 4.9     |
| AC\(_{NH}_4\)ClO\(_4\) | 0.68                  | 256.92                      | 96.28                      | 5.1     |
| AC\(_{1h}\)      | 1.09                  | 194.63                      | 93.65                      | 3.2     |
| AC\(_{NH}_4\)NO\(_3\)\(_{1h}\) | 0.93                  | 220.33                      | 94.07                      | 3.8     |
| AC\(_{NH}_4\)ClO\(_4\)\(_{1h}\) | 0.97                  | 212.37                      | 94.17                      | 3.6     |
| AC\(_{2h}\)      | 1.03                  | 169.21                      | 81.10                      | 3.4     |
| AC\(_{NH}_4\)NO\(_3\)\(_{2h}\) | 1.01                  | 202.89                      | 91.47                      | 3.5     |
| AC\(_{NH}_4\)ClO\(_4\)\(_{2h}\) | 0.95                  | 201.71                      | 90.14                      | 3.7     |
| AC\(_{3h}\)      | 1.09                  | 179.18                      | 83.17                      | 3.2     |
| AC\(_{NH}_4\)NO\(_3\)\(_{3h}\) | 1.09                  | 191.59                      | 87.11                      | 3.2     |
| AC\(_{NH}_4\)ClO\(_4\)\(_{3h}\) | 1.09                  | 193.59                      | 89.99                      | 3.2     |

3.3. Surface Chemical Composition

Table 6 summarizes the surface composition of the prepared ACs, determined by XPS analysis. Hydrogen is also present in the chemical composition of the ACs, but it cannot be detected by XPS.

Table 6. Surface chemical composition, determined using XPS, for the obtained activated carbons.

| Sample                 | Concentration [at. %] |
|------------------------|-----------------------|
|                        | C  | O  | N  |
| AC                     | 87 | 13 | 0  |
| AC\(_{1h}\)           | 97 | 3  | 0  |
| AC\(_{2h}\)           | 97 | 3  | 0  |
| AC\(_{3h}\)           | 96 | 4  | 0  |
| AC\(_{NH}_4\)NO\(_3\) | 88 | 9  | 3  |
| AC\(_{NH}_4\)NO\(_3\)\(_{1h}\) | 91 | 6  | 3  |
| AC\(_{NH}_4\)NO\(_3\)\(_{2h}\) | 89 | 8  | 3  |
| AC\(_{NH}_4\)NO\(_3\)\(_{3h}\) | 87 | 9  | 4  |
| AC\(_{NH}_4\)ClO\(_4\) | 90 | 7  | 3  |
| AC\(_{NH}_4\)ClO\(_4\)\(_{1h}\) | 91 | 8  | 2  |
| AC\(_{NH}_4\)ClO\(_4\)\(_{2h}\) | 90 | 8  | 2  |
| AC\(_{NH}_4\)ClO\(_4\)\(_{3h}\) | 85 | 13 | 3  |

Based on the surface chemical composition analysis by XPS, it can be noted that the preparation of ACs with this procedure, which includes the precursor ‘doping’ with \( NH_4NO_3 \) or \( NH_4ClO_4 \), is suitable for the incorporation of nitrogen heteroatoms in the composition of the ACs. Thus, the corresponding \( NH_4NO_3 \) and \( NH_4ClO_4 \)-ACs contain 2–4 at. % of nitrogen on their surface and the concentrations of nitrogen are similar for both \( NH_4NO_3 \) and \( NH_4ClO_4 \) series.

These ACs also possess noticeable surface oxygen contents. The highest concentration of oxygen was exhibited by the sample named AC. Comparing the just-carbonized \( NH_4NO_3 \) and \( NH_4ClO_4 \) series, it can be observed that sample AC\(_{NH}_4\)NO\(_3\) has a higher concentration of oxygen than AC\(_{NH}_4\)ClO\(_4\). Further activation of the \( NH_4NO_3 \) series leads to lower oxygen concentration than in the case of the \( NH_4ClO_4 \) series. Chlorine is not detected in the AC\(_{NH}_4\)ClO\(_4\) obtained materials. It is assumed that it was removed as a gaseous byproduct during the carbonization process.

The XPS signals of carbon, oxygen, and nitrogen have allowed determining the type and the concentration of functional groups appearing on the surface of the obtained activated carbons. They are presented in Figure 6.
Figure 6. Carbon functional groups (a–c), oxygen functional groups (d–f), nitrogen functional groups (g,h) on the surface of the obtained activated carbons.

Functional groups containing carbon were identified based on the following binding energies: C-C 284.6 ± 0.3 eV, C-O 286.1 ± 0.3 eV, keto-enolic 286.4 ± 0.3 eV, C=O 287.6 ± 0.3 eV, COOH 289.1 ± 0.3 eV and π-π* (satellite peak of carbon in aromatic compounds, C-C with sp² hybridization) 292.15 ± 2.15 eV. The full width at half maximum (FWHM) was set at the same value for each functional group, except for the satellite peak. In the case of O 1s signal, binding energies for particular components were: C=O 531.1 ± 0.3 eV, C-O 532.8 eV ± 0.3 eV, COOH 534.2 ± 0.3 eV, N=O 535.2 ± 0.3 eV, and gas phase H₂O 536.1 ± 0.3 eV. Nitrogen functional groups were determined based on the
following binding energies: pyridinic N-6 397.8 ± 0.3 eV, pyrrolic N-5 399.9 ± 0.3 eV, quaternary N-Q 401.2 ± 0.3 eV, and nitrogen oxides N-O 402.2 ± 0.3 eV. In the case of O 1s and N 1s, full width at maximum (FWHM) was set at the same value for each component.

Based on the deconvolution of C 1s, O 1s, and N 1s signals, it can be observed that the obtained AC series contain mainly C-C (sp\(^3\) and sp\(^2\) hybridization) and C-O bonds.

The exception is sample AC, which also contains COOH groups. However, after activation processes, COOH groups decomposed into C=O and C-O bonds. It is assumed that the high concentration of COOH groups is associated with maleic acid, used as a catalyst during polycondensation reactions to prepare the precursor.

In the case of carbons derived from doped-precursors, the addition of NH\(_4\)NO\(_3\) caused a substantial increase in the content of C=O groups and a decrease of C-O groups. In the case of the NH\(_4\)ClO\(_4\) series, it led to lower concentrations of C=O groups in comparison to the AC series and NH\(_4\)NO\(_3\) series. On the other hand, the NH\(_4\)ClO\(_4\)-activated carbons are characterized by higher C-O groups concentration than the NH\(_4\)NO\(_3\)-activated carbons.

In the case of nitrogen functional groups, NH\(_4\)NO\(_3\)- and NH\(_4\)ClO\(_4\)-modified activated carbons contain mainly pyridinic (N-6) and nitrogen oxide (N-O) groups. Quaternary nitrogen (N-Q) only appears in samples prepared by carbonization.

Moreover, NH\(_4\)NO\(_3\)-activated carbons contain pyrrolic nitrogen (N-5), which is not present in NH\(_4\)ClO\(_4\)-activated carbons. Focusing on the quaternary nitrogen concentration, in the NH\(_4\)NO\(_3\) series it is higher than in the NH\(_4\)ClO\(_4\) series.

3.4. Thermal Stability

Figure 7 compiles the DTG data for either samples obtained after carbonization or after carbonization and activation for 1 h.

![Figure 7](image_url)

Figure 7. DTG data for determining thermal stability for (a) carbons only after carbonization, (b) carbons after 1 h activation.

In the samples carbonized at 600 °C two peaks, attributed to the removal of volatile organic compounds and adsorbed moisture, appear at low temperatures. The third peak, appearing between 550 °C and 780 °C, helps to understand the stability temperature of the carbonized activated carbons. The DTG data shows that after 1 h activation process, activated carbons have comparable thermal stabilities. Thus, the addition of the NH\(_4\)NO\(_3\) or NH\(_4\)ClO\(_4\) during the synthesis of the precursor does not modify the thermal stability of the obtained samples.

It is worth highlighting that these loss peaks correspond to the COOH groups removal, which is confirmed by the XPS analysis.
3.5. CO$_2$ and C$_2$H$_4$ Adsorption

CO$_2$ and C$_2$H$_4$ sorption capacities were measured at a temperature of 30 °C. In Figure 8, these capacities are presented.

Figure 8 shows that for all the activated carbons, the C$_2$H$_4$ sorption capacity is substantially higher than that of CO$_2$. The carbonized materials show similar and lower CO$_2$ and C$_2$H$_4$ uptakes (~1.3 mmol/g). The highest adsorption of CO$_2$ was exhibited by the sample AC$_{\text{NH}_4\text{NO}_3\_1h}$ (2.2 mmol/g). In the unmodified AC series, the highest sorption capacity of CO$_2$ was exhibited by the sample AC$_{2h}$ (2.1 mmol/g). So, the incorporation of NH$_4$NO$_3$ to the precursor has led to an increase in the sorption properties. The highest C$_2$H$_4$ adsorption was reached by the samples AC$_{2h}$ and AC$_{\text{NH}_4\text{NO}_3\_1h}$. It was 3.4 mmol/g.

These results highlight that the incorporation of NH$_4$NO$_3$ into the composition of the precursor permits to shorten the activation time: it leads to optimized materials towards CO$_2$ and C$_2$H$_4$ sorption capacities for the prepared ACs are similar to those from the literature for biomass-derived activated carbons. For instance, Zhang and co-workers produced carbon adsorbents from soybean straw via pyrolysis at 500 °C followed by CO$_2$ activation at 900 °C [71]. As a result, CO$_2$ uptake at 30 °C reached 1.5 mmol/g.

Xiong et al. prepared activated carbons from cotton stalks by CO$_2$ activation at 900 °C [72]. The achieved sorption capacity of CO$_2$ at 20 °C was 1.8 mmol/g. On the other hand, Lahijani proposed the preparation of activated carbons from walnut shells via pyrolysis at 900 °C and modification with magnesium [73]. In their case, CO$_2$ uptake at 25 °C reached 1.9 mmol/g.

Wang et al. obtained carbonaceous materials for the C$_2$H$_4$ adsorption using hardwood ligninosulfate as a precursor [74]. The highest C$_2$H$_4$ uptake was reached by the sample obtained after pyrolysis at 800 °C. It was 2.2 mmol/g at 25 °C. Ye and co-workers measured the sorption capacities of C$_2$H$_4$ and propylene (C$_3$H$_6$) for 15 commercial activated carbons [75]. In the case of C$_2$H$_4$, the highest uptake was 3.1 mmol/g.
4. Conclusions

The purpose of this study was to examine the influence of NH$_4$NO$_3$ and NH$_4$ClO$_4$ added during the preparation of a furfuryl-derived precursor on the preparation of ACs by “carbonization” followed by CO$_2$ activation. It has been shown that the addition of NH$_4$NO$_3$ to the precursor’s composition has led to an important porosity enhancement, with specific surface areas up to 1523 m$^2$/g, micropore volumes up to 0.41 cm$^3$/g, mesopore volumes up to 0.29 cm$^3$/g (and some slight increase in narrow microporosity for a low activation time).

The incorporation of NH$_4$NO$_3$ and NH$_4$ClO$_4$ does not influence the thermal stability of the prepared carbons but modifies the composition of the surface groups. Thus, an advantage of these modified ACs is that they present surface nitrogen contents between 2–4 at. % and they maintain high surface oxygen contents. The type and contribution of nitrogen species are dependent on the preparation conditions. Quaternary nitrogen only appears in doped samples prepared by carbonization, being larger for NH$_4$NO$_3$. NH$_4$NO$_3$-activated carbons contain pyrrolic nitrogen, not present in NH$_4$ClO$_4$-activated carbon, and both NH$_4$NO$_3$- and NH$_4$ClO$_4$-modified activated carbons contain pyridinic and nitrogen oxide groups.

The prepared ACs present a good structural order, derived from the corresponding carbonized materials. Comparing the influence of the doping salts, carbons in NH$_4$NO$_3$ series are characterized by a more disordered structure than from the NH$_4$ClO$_4$ series, presenting both series of samples higher disordered structure than the one prepared from the undoped polymer.

The highest adsorption of CO$_2$ was exhibited by the sample AC$_{\text{NH}_4\text{NO}_3\_1h}$ (2.2 mmol/g). In the unmodified AC series, the highest sorption capacity of CO$_2$ was exhibited by the sample AC$_{\text{NH}_4\text{NO}_3\_2h}$ (2.1 mmol/g). The highest C$_2$H$_4$ adsorption was reached by the samples AC$_{\text{NH}_4\text{NO}_3\_1h}$ and AC$_{\text{NH}_4\text{NO}_3\_2h}$. It was 3.4 mmol/g. These two ACs present the largest amount of micropores with a mean diameter of around 0.5–0.7 nm, particularly interesting for these applications.

NH$_4$NO$_3$ is commonly used as a fertilizer and its cost is relatively low. The precursor’s modification with NH$_4$NO$_3$ reduces the activation time from 2 h to 1 h, with the consequent reduction of the production costs, leading to activated carbons with comparable sorption capacities of CO$_2$ and C$_2$H$_4$ to carbons derived from undoped precursors.

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References

1. Alahabadi, A.; Singh, P.; Raizada, P.; Anastopoulos, I.; Sivamani, S.; Dotto, G.L.; Landarani, M.; Ivanets, A.; Kyzas, G.Z.; Hosseini-Bandegharaei, A. Activated Carbon from Wood Wastes for the Removal of Uranium and Thorium Ions through Modification with Mineral Acid. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *607*, 125516. [CrossRef]

2. Danish, M.; Ahmad, T. A Review on Utilization of Wood Biomass as a Sustainable Precursor for Activated Carbon Production and Application. *Renew. Sustain. Energy Rev.* **2018**, *87*, 1–21. [CrossRef]
3. Asrat, Y.; Adugna, A.T.; Kamraj, M.; Beyan, S.M. Adsorption Phenomenon of Arundinia Alpina Stem-Based Activated Carbon for the Removal of Lead from Aqueous Solution. J. Chem. 2021, 2021, 5554353. [CrossRef]

4. Ali, I.; Afshinb, S.; Poureshgh, Y.; Azari, A.; Rashibari, Y.; Feizizadeh, A.; Hamzezadeh, A.; Fazlizadeh, M. Green Preparation of Activated Carbon from Pomegranate Peel Coated with Zero-Valent Iron Nanoparticles (NZVI) and Isothermal and Kinetic Studies of Amoxicillin Removal in Water. Environ. Sci. Pollut. Res. 2020, 27, 36732–36743. [CrossRef]

5. Foo, K.Y.; Hameed, B.H. Preparation, Characterization and Evaluation of Adsorptive Properties of Orange Peel Based Activated Carbon via Microwave Induced K$_2$CO$_3$ Activation. Bioresour. Technol. 2012, 104, 679–686. [CrossRef] [PubMed]

6. Huang, G.; Liu, Y.; Wu, X.; Cai, J. Activated Carbons Prepared by the KOH Activation of a Hydrochar from Garlic Peel and Their CO$_2$ Adsorption Performance. New Carbon Mater. 2019, 34, 247–257. [CrossRef]

7. Zheng, L.; Wang, S.; Yang, Y.; Fu, X.; Jiang, T.; Yang, J. Ammonium Nitrate-Assisted Synthesis of Nitrogen/Sulfur-Codoped Hierarchically Porous Carbons Derived from Ginkgo Leaf for Supercapacitors. ACS Omega 2019, 4, 5904–5914. [CrossRef]

8. Lucas, W.J.; Groover, A.; Lichtenberger, R.; Furuta, K.; Yadav, S.-R.; Helariutta, Y.; He, X.-Q.; Fukuda, H.; Kang, J.; Brady, S.M.; et al. The Plant Vascular System: Evolution, Development and Functions. J. Integr. Plant Biol. 2013, 55, 294–388. [CrossRef] [PubMed]

9. Matsuzawa, F.; Amano, Y.; Machida, M. Phosphate Ion Adsorption Characteristics of PAN-Based Activated Carbon Prepared by Zinc Chloride Activation. Int. J. Environ. Sci. Technol. 2022, 19, 8159–8168. [CrossRef]

10. László, K.; Szűcs, A. Surface Characterization of Polyethyleneterephthalate (PET) Based Activated Carbon and the Effect of PH on Its Adsorption Capacity from Aqueous Phenol and 2,3,4-Trichlorophenol Solutions. Carbon 2001, 39, 1945–1953. [CrossRef]

11. Alcañiz-Monge, J.; Román-Martínez, M.d.C.; Lillo-Ródenas, M.A. Chemical Activation of Lignocellulosic Precursors and Residues: What Else to Consider? Molecules 2022, 27, 1630. [CrossRef] [PubMed]

12. Hu, S.; Jiang, L.; Wang, Y.; Su, S.; Sun, L.; Xu, B.; He, L.; Xiang, J. Effects of Inherent Alkali and Alkaline Earth Metallic Species on Biomass Pyrolysis at Different Temperatures. Bioresour. Technol. 2015, 192, 23–30. [CrossRef] [PubMed]

13. Zhou, L.; Zhang, G.; Reinmöller, M.; Meyer, B. Effect of Inherent Mineral Matter on the Co-Pyrolysis of Highly Reactive Brown Coal and Wheat Straw. Fuel 2019, 239, 1194–1203. [CrossRef]

14. Gesikiewicz-Puchalska, A.; Zgrzebnicki, M.; Michalkiewicz, B.; Narkiewicz, U.; Morawski, A.W.; Wrobel, R.J. Improvement of CO$_2$ Uptake of Activated Carbons by Treatment with Mineral Acids. Chem. Eng. J. 2017, 309, 159–171. [CrossRef]

15. Zhang, Y.; Song, X.; Zhang, P.; Gao, H.; Ou, C.; Kong, X. Production of Activated Carbons from Four Wastes via One-Step Activation and Their Applications in Pb$^{2+}$ Adsorption: Insight of Ash Content. Chemosphere 2020, 245, 125587. [CrossRef]

16. Zhang, X.-Y.; Xu, Z.-H.; Zong, M.-H.; Wang, C.-F.; Li, N. Selective Synthesis of Furfuryl Alcohol from Biomass-Derived Furfural Using Immobilized Yeast Cells. Catalysts 2019, 9, 70. [CrossRef]

17. Cao Nhien, L.; Van Duc Long, N.; Kim, S.; Lee, M. Novel Reaction-Hybrid-Extraction-Distillation Process for Furfuryl Alcohol Production from Raw Bio-Furfural. Biochem. Eng. J. 2019, 148, 143–151. [CrossRef]

18. Principe, M.; Martínez, R.; Ortiz, P.; Riemont, J. The Polymerization of Furfuryl Alcohol with P-Toluenesulfonic Acid: Photocross-Linkable Feature of the Polymer. Polímeros 2000, 10, 08–14. [CrossRef]

19. Dubinsky, J.; Zagars, A.; Snidvongs, S.; Hirunlabh, J. Furfuryl Alcohol Made from Agriculture Waste Review. In Proceedings of the Third National and the Fourth Academic Symposium Innovation and Technology for Social Development, Bangkok, Thailand, 23 July 2018.

20. Arnaiz, M.; Nair, V.; Mitra, S.; Ajuria, J. Furfuryl Alcohol Derived High-End Carbons for Ultrafast Dual Carbon Lithium Ion Capacitors. Electrochim. Acta 2019, 304, 437–446. [CrossRef]

21. Zgrzebnicki, M.; Nair, V.; Mitra, S.; Kalamaga, A.; Przepiórski, J.; Wrobel, R.J. N-Doped Activated Carbon Derived from Furfuryl Alcohol—Development of Porosity, Properties, and Adsorption of Carbon Dioxide and Ethene. Chem. Eng. J. 2022, 427, 131709. [CrossRef]

22. Jiang, C.; Yakaboylu, G.A.; Yumak, T.; Zondo, J.W.; Sabolsky, E.M.; Wang, J. Activated Carbons Prepared by Indirect and Direct CO$_2$ Activation of Lignocellulosic Waste by Treatment with Supercapacitor Electrodes. Renew. Energy 2020, 155, 38–52. [CrossRef]

23. Ouyang, J.; Zhou, L.; Liu, Z.; Heng, J.Y.Y.; Chen, W. Biomass-Derived Activated Carbons for the Removal of Pharmaceutical Micropol lutants from Wastewater: A Review. Sep. Purif. Technol. 2020, 253, 117536. [CrossRef]

24. Moreno-Castilla, C.; Carrasco-Marrn, F.; Lopez-Ramon, M.V.; Alvarez-Merino, M.A. Chemical and Physical Activation of Olive-Mill Water Waste to Produce Activated Carbons. Carbon 2001, 39, 1415–1420. [CrossRef]

25. Şahin, Ö.; Saka, C. Preparation and Characterization of Activated Carbon from Acorn Shell by Physical Activation with H$_2$O–CO$_2$ in Two-Step Pretreatment. Bioresour. Technol. 2013, 136, 163–168. [CrossRef]

26. Hassan, M.F.; Sabri, M.A.; Fazal, H.; Hafteez, A.; Shezad, N.; Hussain, M. Recent Trends in Activated Carbon Fibers Production from Various Precursors and Applications—A Comparative Review. J. Anal. Appl. Pyrolysis 2020, 145, 104715. [CrossRef]

27. Jajgwe, J.; Olopot, P.W.; Menya, E.; Kalibbala, H.M. Synthesis and Application of Granular Activated Carbon from Biomass Waste Materials for Water Treatment: A Review. J. Bioresour. Bioprod. 2021, 6, 292–322. [CrossRef]

28. Kosheleva, R.I.; Mitropoulos, A.C.; Kyzys, G.Z. Synthesis of Activated Carbon from Food Waste. Environ. Chem. Lett. 2019, 17, 429–438. [CrossRef]

29. Heidarinejad, Z.; Dehghani, M.H.; Heidari, M.; Javedan, G.; Ali, I.; Sillanpää, M. Methods for Preparation and Activation of Activated Carbon: A Review. Environ. Chem. Lett. 2020, 18, 393–415. [CrossRef]

30. Rashidi, N.A.; Yusup, S. Production of Palm Kernel Shell-Based Activated Carbon by Direct Physical Activation for Carbon Dioxide Adsorption. Environ. Sci. Pollut. Res. 2020, 26, 33732–33746. [CrossRef]
31. Olivas-Marin, M.; Fernandez-Gonzalez, C.; Macias-Garcia, A.; Gomez-Serrano, V. Preparation of Activated Carbon from Cherry Stones by Physical Activation in Air. Influence of the Chemical Carbonisation with H_2SO_4. J. Anal. Appl. Pyrolysis 2012, 94, 131–137. [CrossRef]

32. Rodriguez-Reinoso, F.; Molina-Sabio, M.; Gonzalez, M.T. The use of steam and CO_2 as activating agents in the preparation of activated carbons. Carbon 1995, 33, 15–23. [CrossRef]

33. Ao, W.; Fu, J.; Mao, X.; Kang, Q.; Ran, C.; Liu, Y.; Zhang, H.; Gao, Z.; Li, J.; Liu, G.; et al. Microwave Assisted Preparation of Activated Carbon from Biomass: A Review. Renew. Sustain. Energy Rev. 2018, 82, 958–979. [CrossRef]

34. Liew, R.K.; Azwar, E.; Yek, P.N.Y.; Lim, X.Y.; Cheng, C.K.; Ng, J.H.; Jusoh, A.; Lam, W.H.; Ibrahim, M.D.; Ma, N.L.; et al. Microwave Pyrolysis with KOH/NaOH Mixture Activation: A New Approach to Produce Micro-Mesoporous Activated Carbon for Textile Dye Adsorption. Bioresour. Technol. 2018, 266, 1–10. [CrossRef] [PubMed]

35. Lee, D.Y.; Choi, J.H.; Shin, J.C.; Jung, M.K.; Song, S.K.; Suh, J.K.; Lee, C.Y. Plasma Functionalization of Powdery Nanomaterials Using Porous Filter Electrode and Sample Circulation. Appl. Surf. Sci. 2018, 443, 628–634. [CrossRef]

36. Ortiz-Ortega, E.; Hosseini, S.; Martinez-Chapa, S.O.; Madou, M.J. Aging of Plasma-Activated Carbon Surfaces: Challenges and Opportunities. Appl. Surf. Sci. 2021, 565, 105362. [CrossRef]

37. Zhang, W.; Yang, P.; Luo, M.; Wang, X.; Zhang, T.; Chen, W.; Zhou, X. Fast Oxygen, Nitrogen Co-Functionalization on Electrospun Lignin-Based Carbon Nanofibers Membrane via Air Plasma for Energy Storage Application. Int. J. Biol. Macromol. 2020, 143, 434–442. [CrossRef]

38. Chen, W.; Gong, M.; Li, K.; Xia, M.; Chen, Z.; Xiao, H.; Fang, Y.; Chen, Y.; Yang, H.; Chen, H. Insight into KOH Activation Mechanism during Biomass Pyrolysis: Chemical Reactions between O-Containing Groups and KOH. Appl. Energy 2020, 278, 115730. [CrossRef] [PubMed]

39. Li, S.; Han, K.; Li, J.; Li, M.; Lu, C. Preparation and Characterization of Super Activated Carbon Produced from Gullweed by KOH Activation. Microporous Mesoporous Mater. 2017, 243, 291–300. [CrossRef]

40. Sevilla, M.; Ferrero, G.A.; Fuertes, A.B. Beyond KOH Activation for the Synthesis of Superactivated Carbons from Hydrochar. Progress Nat. Sci. Mater. Int. 2019, 114, 50–58. [CrossRef]

41. Muniandy, L.; Adam, F.; Mohamed, A.R.; Ng, E.-P. The Synthesis and Characterization of High Purity Mixed Microporous/Mesoporous Activated Carbon from Rice Husk Using Chemical Activation with NaOH and KOH. Microporous Mesoporous Mater. 2014, 197, 316–323. [CrossRef]

42. Singha, J.; Bhunia, H.; Basu, S. Adsorption of CO_2 on KOH Activated Carbon Adsorbents: Effect of Different Mass Ratios. J. Environ. Manag. 2019, 250, 109457. [CrossRef] [PubMed]

43. Le Van, K.; Luong Thi, T.T. Activated Carbon Derived from Rice Husk by NaOH Activation and Its Application in Supercapacitor. Progress Nat. Sci. Mater. Int. 2014, 24, 191–198. [CrossRef]

44. Xu, B.; Chen, Y.; Wei, G.; Cao, G.; Zhang, H.; Yang, Y. Activated Carbon with High Capacitance Prepared by NaOH Activation for Supercapacitors. Mater. Chem. Phys. 2010, 124, 504–509. [CrossRef]

45. Liu, J.; Yang, X.; Liu, H.; Cheng, W.; Bao, Y. Modification of Calcium-Rich Biochar by Loading Si/Mn Binary Oxide after NaOH Activation and Its Adsorption Mechanisms for Removal of Cu(II) from Aqueous Solution. Colloids Surf. A Physicochem. Eng. Asp. 2020, 601, 124960. [CrossRef]

46. Dawei, L.; Yu, W.; Jiaojiao, Z.; Jicheng, W.; Xiaoyang, L.; Yuanwu, Y.; Zongbo, Z.; Yingyun, Q.; Ling, W.; Junhua, L.; et al. Drying before Microwave-Assisted H_3PO_4 Activation to Produce Highly Mesoporous Activated Carbons. Mater. Lett. 2018, 230, 61–63. [CrossRef]

47. Yang, Z.; Gleisner, R.; Mann, D.H.; Xu, J.; Jiang, J.; Zhu, J.Y. Lignin Based Activated Carbon Using H_3PO_4 Activation. Polymers 2020, 12, 2829. [CrossRef]

48. Jawad, A.H.; Malek, N.N.A.; Khadiran, T.; ALothman, Z.A.; Yaseen, Z.M. Mesoporous High-Surface-Area Activated Carbon from Biomass Waste via Microwave-Assisted-H_3PO_4 Activation for Methylene Blue Dye Adsorption: An Optimized Process. Diam. Relat. Mater. 2022, 128, 109289. [CrossRef]

49. Vinain, E.; Njewa, J.B.; Biswick, T.T.; Ipaideola, A.K. Adsorption of Chromium Ions from Tannery Effluents onto Activated Carbon Prepared from Rice Husk and Potato Peel by H_3PO_4 Activation. Appl. Water Sci. 2021, 11, 150. [CrossRef]

50. Uçar, S.; Erdem, M.; Tay, T.; Karagöz, S. Preparation and Characterization of Activated Carbon Produced from Pomegranate Seeds by ZnCl_2 Activation. Appl. Surf. Sci. 2009, 255, 8890–8896. [CrossRef]

51. Nakagawa, Y.; Molina-Sabio, M.; Rodriguez-Reinoso, F. Modification of the Porous Structure along the Preparation of Activated Carbon Monoliths with H_3PO_4 and ZnCl_2. Microporous Mesoporous Mater. 2007, 103, 29–34. [CrossRef]

52. Wang, T.; Tan, S.; Liang, C. Preparation and Characterization of Activated Carbon from Wood via Microwave-Induced ZnCl_2 Activation. Carbon 2009, 47, 1880–1883. [CrossRef]

53. Sakamoto, T.; Amano, Y.; Machida, M. Phosphate Ion Adsorption Properties of PAN-Based Activated Carbon Fibers Prepared with K_2CO_3 Activation. SN Appl. Sci. 2020, 2, 702. [CrossRef]

54. Sajjadi, S.-A.; Mohammadzadeh, A.; Tran, H.N.; Anastopoulos, I.; Dotto, G.L.; Lopitić, Z.R.; Sivamani, S.; Rahmani-Sani, A.; Ivanets, A.; Hosseini-Bandegharaei, A. Efficient Mercury Removal from Wastewater by Pistachio Wood Wastes-Derived Activated Carbon Prepared by Chemical Activation Using a Novel Activating Agent. J. Environ. Manag. 2018, 223, 1001–1009. [CrossRef]

55. Fu, K.; Yue, Q.; Gao, B.; Wang, Y.; Li, Q. Activated Carbon from Tomato Stem by Chemical Activation with FeCl_3. Colloids Surf. A Physicochem. Eng. Asp. 2017, 529, 842–849. [CrossRef]

56. Subramanian, N.; Viswanathan, B. Nitrogen- and Oxygen-Containing Activated Carbons from Sucrose for Electrochemical Supercapacitor Applications. RSC Adv. 2015, 5, 63000–63011. [CrossRef]
57. Bayrak, Y.; Topallar, H.; Karagöz, B.; Kılıç, İ. Kinetics and Thermodynamics of Cr(VI), Cu(II), and Ni(II) Adsorption on Activated Carbon Prepared from Rice Hulls. *J. Dispers. Sci. Technol.* 2013, **34**, 1248–1256. [CrossRef]

58. Sajjadi, S.-A.; Meknati, A.; Lima, E.C.; Dotto, G.L.; Mendoza-Castillo, D.I.; Anastopoulos, I.; Alakhras, F.; Unuabonah, E.I.; Singh, P.; Hosseini-Bandegharaei, A. A Novel Route for Preparation of Chemically Activated Carbon from Pistachio Wood for Highly Efficient Pb(II) Sorption. *J. Environ. Manag.* 2019, **236**, 34–44. [CrossRef]

59. Ma, X.-Q.; Zhang, B.; Xu, Z.-X.; Tan, Y.; Li, B.; Zhang, Y.-C.; Ni, G.-S.; Zhou, W.-Y.; Luque, R.; Zhang, H.-Y. N-Rich and O-Poor Doped Carbon Prepared via Facile Ammonium Nitrate Assisted Hydrothermal Carbonization for Robust Supercapacitors. *J. Clean. Prod.* 2022, **373**, 133903. [CrossRef]

60. Boldyrev, V.V. Thermal Decomposition of Ammonium Perchlorate. *Thermochim. Acta* 2006, **443**, 1–36. [CrossRef]

61. Sharma, J.K.; Srivastava, P.; Singh, G.; Akhtar, M.S.; Ameen, S. Catalytic Thermal Decomposition of Ammonium Perchlorate and Combustion of Composite Solid Propellants over Green Synthesized CuO Nanoparticles. *Thermochim. Acta* 2015, **614**, 110–115. [CrossRef]

62. Xie, Y.; Wang, Y.; Giammar, D.E. Impact of Chlorine Disinfectants on Dissolution of the Lead Corrosion Product PbO₂. *Environ. Sci. Technol.* 2010, **44**, 7082–7088. [CrossRef] [PubMed]

63. Raza, A.; Gholami, R.; Rezaee, R.; Rasouli, V.; Rabiei, M. Significant Aspects of Carbon Capture and Storage—A Review. *Petroleum* 2019, **5**, 335–340. [CrossRef]

64. Chen, Y.; Grimplet, J.; David, K.; Castellarin, S.D.; Terol, J.; Wong, D.C.J.; Luo, Z.; Schaffer, R.; Celton, J.-M.; Talon, M.; et al. Ethylene Receptors and Related Proteins in Climacteric and Non-Climacteric Fruits. *Plant Sci.* 2018, **276**, 63–72. [CrossRef] [PubMed]

65. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* 2015, **87**, 1051–1069. [CrossRef]

66. Puech, P.; Dabrowska, A.; Ratel-Ramond, N.; Vignoles, G.L.; Monthioux, M. New Insight on Carbonisation and Graphitisation Mechanisms as Obtained from a Bottom-up Analytical Approach of X-Ray Diffraction Patterns. *Carbon* 2019, **147**, 602–611. [CrossRef]

67. Fujimoto, H. Theoretical X-Ray Scattering Intensity of Carbons with Turbostratic Stacking and AB Stacking Structures. *Carbon* 2003, **41**, 1585–1592. [CrossRef]

68. Cançado, L.G.; Takai, K.; Enoki, T.; Endo, M.; Kim, Y.A.; Mizusaki, H.; Jorio, A.; Coelho, L.N.; Magalhães-Paniago, R.; Pimenta, M.A. General Equation for the Determination of the Crystallite Size La of Nanographite by Raman Spectroscopy. *Appl. Phys. Lett.* 2006, **88**, 163106. [CrossRef]

69. Zhao, Z.; Dai, Y.; Ge, G. Nitrogen-Doped Nanotubes-Decorated Activated Carbon-Based Hybrid Nanoarchitecture as a Superior Catalyst for Direct Dehydrogenation. *Catal. Sci. Technol.* 2015, **5**, 1548–1557. [CrossRef]

70. Kumar, N.; Srivastava, V.C. Simple Synthesis of Large Graphene Oxide Sheets via Electrochemical Method Coupled with Oxidation Process. *ACS Omega* 2018, **3**, 10233–10242. [CrossRef]

71. Zhang, X.; Wu, J.; Yang, H.; Shao, J.; Wang, X.; Chen, Y.; Zhang, S.; Chen, H. Preparation of Nitrogen-Doped Microporous Modified Biochar by High Temperature CO₂-NH₃ Treatment for CO₂ Adsorption: Effects of Temperature. *RSC Adv.* 2016, **6**, 98157–98166. [CrossRef]

72. Xiong, Z.; Shihong, Z.; Haiping, Y.; Tiao, S.; Yingquan, C.; Hanping, C. Influence of NH₃/CO₂ Modification on the Characteristic of Biochar and the CO₂ Capture. *Bioenerg. Res.* 2013, **6**, 1147–1153. [CrossRef]

73. Lahijani, P.; Mohammadi, M.; Mohamed, A.R. Metal Incorporated Biochar as a Potential Adsorbent for High Capacity CO₂ Capture at Ambient Condition. *J. CO₂ Util.* 2018, **26**, 281–293. [CrossRef]

74. Wang, S.-H.; Hwang, Y.-K.; Choi, S.W.; Yuan, X.; Lee, K.B.; Chang, F.C. Developing Self-Activated Lignosulfonate-Based Porous Carbon Material for Ethylene Adsorption. *J. Taiwan Inst. Chem. Eng.* 2020, **115**, 315–320. [CrossRef]

75. Ye, P.; Fang, Z.; Su, B.; Xing, H.; Yang, Y.; Su, Y.; Ren, Q. Adsorption of Propylene and Ethylene on 15 Activated Carbons. *J. Chem. Eng. Data* 2010, **55**, 5669–5672. [CrossRef]