

Article

Activated Carbon Ammonization: Effects of the Chemical Composition of the Starting Material and the Treatment Temperature

Silvia da C. Oliveira ¹, Romulo C. Dutra ¹ , José J. L. León ¹ , Gesley A. V. Martins ¹, Alysson M. A. Silva ² , Diana C. S. de Azevedo ³ , Rafaelle G. Santiago ³, Daniel Ballesteros-Plata ⁴ , Enrique Rodríguez-Castellón ^{4,*}  and Marcos J. Prauchner ^{1,*} 

¹ Institute of Chemistry, University of Brasilia, Campus Darcy Ribeiro, Brasilia 70904-970, DF, Brazil; silviaoliveira.sco@gmail.com (S.d.C.O.); romulodutrac@gmail.com (R.C.D.); joselinaires@unb.br (J.J.L.); gesley@unb.br (G.A.V.M.)

² Department of Mechanical Engineering, Faculty of Technology, University of Brasilia, Campus Darcy Ribeiro, Brasilia 70904-970, DF, Brazil; alyssonmartins@unb.br

³ Department of Chemical Engineering, University Federal of Ceará, Campus do Pici, Fortaleza 60760-400, CE, Brazil; diana.azevedo@ufc.br (D.C.S.d.A.); rafaelle.santiago@gpsa.ufc.br (R.G.S.)

⁴ Department of Inorganic Chemistry, Crystallography and Mineralogy, Inter-university Institute of Research in Biorefineries I3B, Faculty of Sciences, University of Málaga, 29071 Málaga, Spain; daniel.ballesteros@uma.es

* Correspondence: castellon@uma.es (E.R.-C.); marcosjp@unb.br (M.J.P.)



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Abstract: N-containing carbon-based materials have been employed with claimed improved performance as an adsorbent of acidic molecules, volatile organic compounds (VOC), and metallic ions; catalyst; electrocatalyst; and supercapacitor. In this context, the present work provides valuable insights into the preparation of N-doped activated carbons (ACs) by thermal treatment in NH₃ atmosphere (ammonization). A commercial AC was submitted to two kinds of pretreatment: (i) reflux with dilute HNO₃; (ii) thermal treatment up to 800 °C in inert atmosphere. The original and modified ACs were subjected to ammonization up to different temperatures. ACs with N content up to ~8% were achieved. Nevertheless, the amount and type of inserted nitrogen depended on ammonization temperature and surface composition of the starting material. Remarkably, oxygenated acidic groups on the surface of the starting material favored nitrogen insertion at low temperatures, with formation of mostly aliphatic (amines, imides, and lactams), pyridinic, and pyrrolic nitrogens. In turn, high temperatures provoked the decomposition of labile aliphatic functions. Therefore, the AC prepared from the sample pre-treated with HNO₃, which had the highest content of oxygenated acidic groups among the materials submitted to ammonization, presented the highest N content after ammonization up to 400 °C but the lowest content after ammonization up to 800 °C.

Keywords: activated carbons; adsorption; surface chemistry; ammonization; N-doped carbons

1. Introduction

Activated carbons (ACs) are nontoxic, inexpensive, and versatile materials that present pronounced porosity and, therefore, large specific surface area (SSA). Thanks to their well-developed and tunable porosity, ACs have been widely applied as adsorbents in gas separation, purification, and storage, water and wastewater treatment, volatile recovery, and removal of noxious substances from biological fluids, as well as a drug carrier for controlled delivery [1–9]. Moreover, other properties, such as good electrical conductivity

and high thermal, chemical, and mechanical resistance make ACs very interesting materials to be used as a catalyst, catalyst support, electrocatalyst, and supercapacitor [10–13].

The arrangement of the carbon skeleton in ACs is complex and variable. However, in general terms, it can be envisaged that they are constituted by small segments of defective graphene layers containing something like five to seven rings, with the valence of edge carbons usually completed by hydrogen. Some of these layers can stack together (not much more than three or four layers) to form such a kind of small graphitic microcrystals. These microdomains are bonded together in a continuous and random way, creating a stable network of carbon atoms. The empty spaces existing throughout the carbon structure correspond to the pores network.

Other elements than carbon or hydrogen can also be present. Oxygen is by far the most common, mainly because it is abundant in most of the usual AC precursors, especially in those derived from biomass, and part of this oxygen remains after the carbonization/activation process. Oxygen can be found in the form of several functional groups, as portrayed in Figure 1, which can be acidic (carboxylic acids, carboxylic anhydrides, lactones, and phenols), nearly neutral (ether and ketones), or basic (as is the case for quinones and pyrones) [14–18].

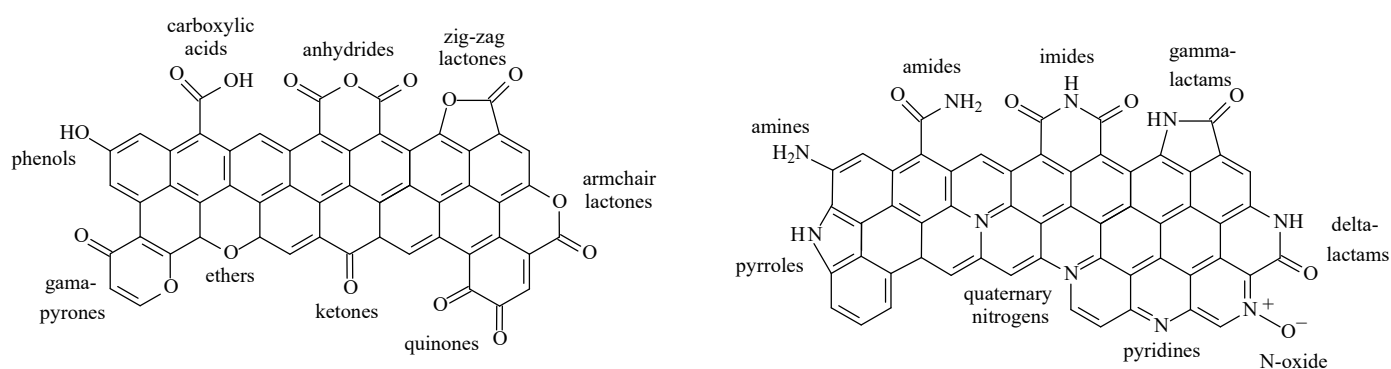


Figure 1. Usual oxygenated and nitrogenated functional groups present in ACs (elaborated considering references [14–20]).

Another heteroatom that has aroused increasing interest is nitrogen, which can be found in the form of functional groups such as those displayed in Figure 1 [16–20]. Since nitrogen is relatively weakly electronegative (if compared to oxygen), the lone electron pair on sp^3 nitrogen (Figure 2a) and pyridine (Figure 2b) is likely to interact with electrophilic entities. Furthermore, in some species, the lone electron pair of N increases the density of π electrons on the basal plane of carbon and gives rise to a positive charge on the nitrogen atom, which enhances the material ability to interact with different species and to transfer electrons in redox reactions. This occurs when nitrogen contributes a pair of electrons for the π system, as is the case for pyrrolic (Figure 2c) and quaternary (also called graphitic) nitrogens (Figure 2d), or even through resonance in aromatic amines (Figure 2e).

Thanks to that, N-containing carbon-based materials (not only ACs but also carbon nanotubes, fullerenes, graphenes, carbon black, carbon foams, etc.) have been employed with claimed improved performance in several applications, such as adsorbent for the separation of acidic molecules such as CO_2 [20–36] and H_2S [37,38] from gaseous mixtures (i.e., biogas, natural gas, industrial exhaust gases, and atmospheric air); adsorbent for the removal of metallic ions [39–44] and organic compounds [7,45] from water; catalyst or catalyst support [17,46–49]; metal-free electrocatalyst and photocatalyst for reactions such as O_2 [10,50–58], CO_2 [59–61], and hydrogen reduction [62,63]; supercapacitor [64–70]; and electrode in metal-ion batteries [71–74], molecular sensors [75,76], and electromagnetic

devices [77,78]. AL-Hajri et al. [9] published a comprehensive review on recent applications of N-doped carbon materials in CO₂ capture and energy conversion and storage.

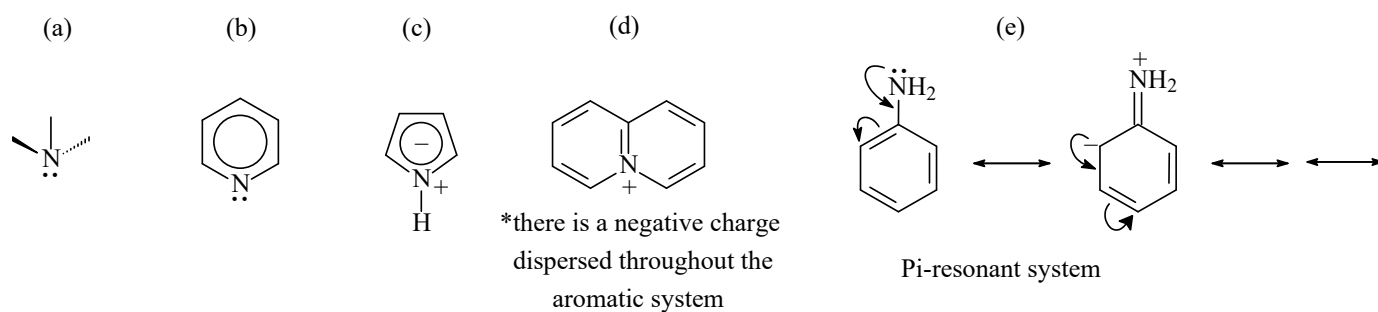


Figure 2. Illustration of the effect provoked by the pair of lone electrons of nitrogen in N-containing carbon-based structures: (a) sp^3 N; (b) pyridinic N; (c) pyrrolic N; (d) quaternary N; (e) resonance in aromatic amines.

N-containing carbon-based materials can be prepared from natural precursors that have considerable content of this element. These are the cases of protein-rich biomasses such as bean dregs [39], yeast [46], chitosan [40], human hair [41], and leather waste [71], in addition to some synthetic polymers and resins [7,21–23,42,47,59,60,62]. Nevertheless, most of the raw materials widely employed for AC production (e.g., coal, coconut shell, wood, etc.) are deficient in nitrogen. Thus, N-containing carbon-based materials can be obtained by mixing conventional N-deficient feedstocks with N-rich substrates such as melamine, urea, and aniline [24–26,37,65]. Chemical vapor deposition (CVD) [50,75,79] and plasma processing [51] of N-rich substrates are less usually employed methodologies. Alternatively, nitrogen can be incorporated through a post-synthesis procedure, usually by heating a mixture of a carbon material in the presence of labile N-containing molecules such as urea and melamine [10,27,28,38,52–54,66,67,76,78] or by exposing a carbon material to a NH_3 atmosphere under heating (ammonization treatment, sometimes also called ammonification or amination) [19,29–33,43,45,48,55,61,68,69,80–83]. Finally, nitrogen molecules such as monoethanolamine and ethylenediamine can be grafted on the surface of carbon-based materials [34,44,64]. The works of Kasera et al. [5], Rashidi et al. [36,70], Li et al. [35], Li et al. [49], Yuan et al. [74], Al-Hajri et al. [9], and Mainali et al. [84] provide comprehensive reviews on the synthesis of N-containing carbon-based materials.

Among the existing techniques, ammonization can be considered one of the most interesting (if not the most) mainly because it imposes no restrictions as to the feedstock and activation methodology. However, there are currently few systematic studies correlating the composition of the starting carbon-based material and the experimental ammonization conditions with the composition and properties of the resulting materials. In this context, the present work aimed to provide new insights into the preparation of N-doped ACs through ammonization and to conciliate these new insights with existing information dispersed in the literature. We therefore hope to contribute to improving the capacity to produce materials with surface properties tailored to specific needs. For that, a biomass-based commercial sample of a hierarchical micro-mesoporous AC (labeled herein WV) was subjected to ammonization up to 400 °C and 800 °C. These temperatures were chosen because, while 400 °C is a relatively low temperature that does not induce significant aromatization, 800 °C is high enough to do so. In addition, the original AC was also submitted to two types of pretreatment: (i) with a HNO_3 solution (nitrification) to increase the material acidity and oxygen content; (ii) a thermal treatment up to 800 °C in an inert atmosphere (complementary carbonization) to reduce the material acidity and oxygen content. Then, the modified ACs (obtained through complementary carbonization or

nitrification) were also subjected to ammonization, so that the influence of the acidic oxygenated functional groups on nitrogen incorporation could be evaluated. The chemical composition of the materials was carefully evaluated through techniques such as X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption coupled with mass spectrometry (TPD-MS), elemental analysis (EA) and Boehm titration, as well as point of zero charge (PZC) measurements. Furthermore, attaining N_2 adsorption/desorption isotherms permitted to evaluate the textural properties.

2. Materials and Methods

2.1. Treatments

A commercial granular activated carbon (WV-A1050, supplied by MeadWestvaco, Richmond, VA, USA) was taken as starting material. According to the producer, the material was obtained from coconut shell (*Cocos nucifera*) by chemical activation with H_3PO_4 . Before any treatment, the material (labeled herein as WV) was dried overnight at 110 °C and then cooled in desiccator with silica gel at room temperature. Figure 3 shows a scheme presenting the performed treatments and the labels attributed to the obtained samples.

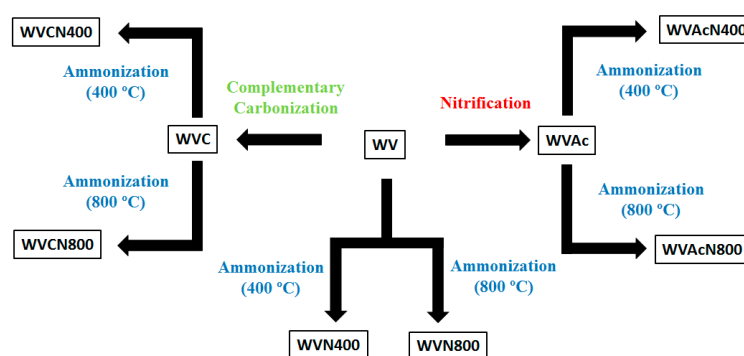


Figure 3. Scheme presenting the performed treatments and respective labels attributed to the obtained samples.

Nitrification was carried out by adding WV (20 g) to a beaker jar containing 200 mL of a 1.0 mol L^{−1} HNO₃ solution. The mixture was kept under reflux (~75 °C) and magnetic stirring for 1 h. After cooling, the material was washed with deionized water until the wash water reached a stable pH of ~6. After that, the obtained material, labeled as WVAc, was dried at 105 °C overnight.

Complementary carbonization and ammonization were carried out in a horizontal furnace equipped with a quartz tube. For carbonization, 8 g of WV were heated to 800 °C (2 h; 5 °C min^{−1}) under inert atmosphere (N₂, 100 mL min^{−1}). The system was then left to cool down to room temperature. The obtained material was labeled as WVC. For ammonization, 8 g of WV, WVC, or WVAc were heated (5 °C min^{−1}) under NH₃ atmosphere (100 mL min^{−1}) to 400 (4 h) or 800 °C (1 h). The atmosphere was then switched to N₂ and the system was left to cool down to room temperature. Initial exploratory ammonization tests were performed to select an adequate holding time at maximum temperature, that is to say, a time period that permitted achieving a N incorporation as high as possible without promoting excessive carbon etching. Based on these tests, 4 and 1 h were adopted as the holding times for ammonization up to 400 and 800 °C, respectively. The obtained samples were labeled as WVN400, WVCN400, WVAcN400, WVN800, WVCN800, and WVAcN800 according to the starting material and the maximum temperature used.

2.2. Materials Characterization

The textural characterization was based on N₂ adsorption/desorption isotherms acquired at −196 °C using an Adsorption Analyzer model Autosorb IQ XR-XR Viton (Anton-Paar, Ashland, VA, USA). Samples were outgassed in situ under vacuum at 150 °C for 8 h before analysis. The apparent SSA and the volume of micropores (V_{mic}) were determined by applying the Brunauer–Emmett–Teller (BET) and Dubinin–Radushkevich (DR) equations, respectively. The volume of liquid N₂ adsorbed at p/p_0 0.95, termed as $V_{0.95}$, was considered the sum of the volumes of micro- and mesopores (V_{mes}). Therefore, V_{mes} was determined by subtracting V_{mic} from $V_{0.95}$. The pore size distribution (PSD) curves were obtained using the software AsiQwin (version 4.0, Quantachrome Instruments, Boynton Beach, FL, USA) and applying the Quenched Solid Density Functional Theory (QSDFT) to the N₂ adsorption data.

The ash content was determined by heating the dried sample to 600 °C (6 h) under atmospheric air in an open muffle furnace. Ash composition was determined by Energy Dispersive X-ray Fluorescence spectroscopy (ED-XRF) using a Shimadzu equipment model EDS 720 HS (Nakagyo-ku, Kyoto, Japan).

C, H, and N contents were measured on a Parkin Elmer CHN Elemental Analyzer model EA 2400 Series II equipped with an AD6 ultra-microbalance (Waltham, MA, USA).

The pH value at which the net charge on a surface is zero is termed the point of zero charge (PZC). It was determined based on an approach widely described in the literature. Eleven solutions with initial pH (pHi) varying in the range from 2 to 12 were prepared by taking 20 mL of 0.100 mol L^{−1} NaCl (background electrolyte) and adjusting the pH with 0.100 mol L^{−1} NaOH or HCl. In total, 20.0 mg of AC were added to each solution and the flasks were shaken for 24 h at room temperature. The final pH of the resulting supernatant liquid (pHf) was measured and the difference between pHi and pHf was plotted against pHi. PZC was identified as the pHi value corresponding to the point where the curve crossed the abscissa axis.

TPD-MS analyses were performed on an automated reaction system model AMI-90R coupled to a Dymaxion quadrupole mass spectrometer (Altamira Instruments, Pittsburgh, PA, USA). The sample (~100.0 mg) was placed in a quartz U-tube under an Ar flow of 10 cm³ min^{−1} at atmospheric pressure and then heated to 100 °C (10 °C min^{−1}) and maintained at this temperature for 60 min to remove water and other adsorbed small molecules. The temperature was then raised to 950 °C using the same heating rate. The evolved gases were continuously monitored with the mass spectrometer. CO and CO₂-profiles were fitted assuming Gaussian distribution for each peak. Peak areas were correlated to the amount of gas through a daily routine calibration that consisted of the injection of a known volume of pure gas using a calibrated loop [16].

The contents of acid and basic groups were determined using a procedure based on the Boehm's titration method [85]. Shortly, the content of basic groups was determined by adding 0.50 g of AC to an Erlenmeyer flask containing 50 mL of a standard HCl solution ~0.100 mol L^{−1}. After magnetic stirring for 24 h and filtration, aliquots of 10 mL of the filtrate were titrated against a standard NaOH solution ~0.100 mol L^{−1}. In turn, the content of acidic groups was determined by back titration; about 0.50 g of AC was added to an Erlenmeyer flask containing 50 mL of the standard NaOH solution. After magnetic stirring for 24 h and filtration, 10 mL aliquots of the filtrate were added to 15 mL of the standard HCl solution. Finally, the excess of acid was titrated against the standard NaOH solution. Blank tests were performed following the same methodology but without the addition of AC. Thus, the contents of acidic or basic groups were determined, taking into account the difference between the volumes of NaOH solution spent to reach the endpoint in the titrations of the sample and the blank. Measurements were taken in triplicate.

XPS measurements were carried out on a Physical Electronics 5700 spectrometer using the Mg-K α line (1253.6 eV) from a PHI model 04-548 Dual Anode X-rays Source (Chanhassen, MN, USA). The X-ray source was run at a power of 300 W (10 keV and 30 mA). The pressure inside the vacuum chamber was 5×10^{-7} Pa. A Perkin Elmer 10-360 hemispherical analyzer (Eden Prairie, MN, USA) was employed with a multi-channel detector. The specimens were analyzed at an angle of 45° to the surface plane. Binding energies (BEs) were referred to the C 1s line of adventitious carbon at 284.8 eV and determined with the resolution of ± 0.1 eV. The spectra were fitted assuming Gaussian–Lorentzian distribution for each peak.

3. Results

3.1. Characterization of the Unmodified AC WV

The N₂ adsorption–desorption isotherms of the unmodified AC WV are displayed in Figure 4a. According to IUPAC classification [86], the adsorption branch can be classified as a hybrid of type I(b) and IV isotherms, which are typical for microporous and mesoporous materials, respectively. This is in accordance with the textural properties compiled in Table 1, where the V_{mic} and V_{mes} for WV were 0.51 and $0.41 \text{ cm}^3 \text{ g}^{-1}$, respectively, with a high SSA of $1506 \text{ m}^2 \text{ g}^{-1}$. The presence of mesopores is confirmed by the occurrence of a prominent hysteresis loop above $p/p_0 \sim 0.4$. This hysteresis loop resembles H4-type, which is associated with slit-shaped pores [86].

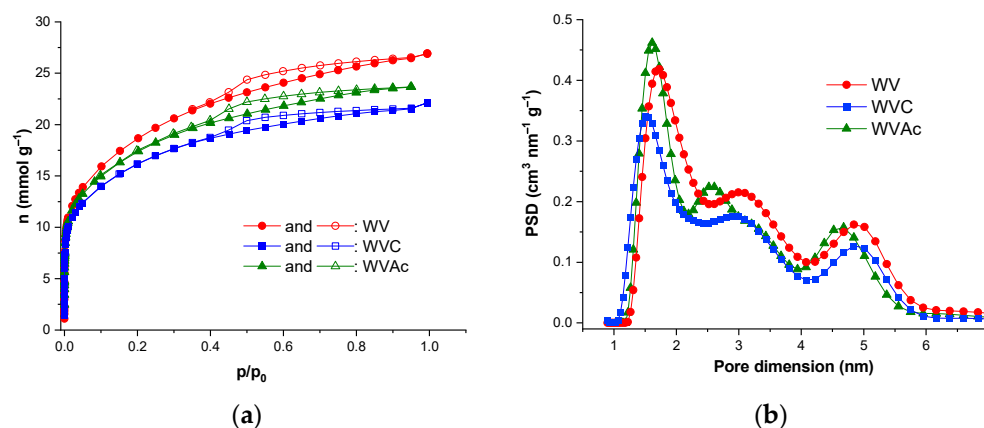


Figure 4. (a) N₂ adsorption–desorption isotherms and (b) corresponding PSD curves (closed and open symbols correspond to the adsorption and desorption branches, respectively).

Table 1. Data of textural characterization (SSA, V_{mic} , $V_{0.95}$, and V_{mes} are defined in Section 2.2).

Sample	SSA ($\text{m}^2 \text{ g}^{-1}$)	V_{mic} ($\text{cm}^3 \text{ g}^{-1}$)	$V_{0.95}$ ($\text{cm}^3 \text{ g}^{-1}$)	V_{mes} ($\text{cm}^3 \text{ g}^{-1}$)
WV	1506	0.51	0.92	0.41
WVN400	1238	0.39	0.72	0.33
WVN800	1247	0.42	0.74	0.32
WVC	1296	0.44	0.75	0.31
WVCN400	1289	0.43	0.74	0.31
WVCN800	1313	0.46	0.76	0.30
WVAc	1392	0.47	0.82	0.35
WVAcN400	1226	0.41	0.72	0.31
WVAcN800	1504	0.50	0.83	0.33

WV presented a relatively high ash content, 4.2 wt%. The ash was analyzed by ED-XRF, which permitted the identification of the following elements and their respective weight percentages (relative to the mass of dry WV before burning): P 1.2; Na 0.7; Si 0.1; and

Ca 0.1 (only elements with a weight percentage ≥ 0.1 were listed here). The presence of some phosphorus is due to the chemical activating agent (H_3PO_4) [28,44,64,87], while the metallic elements must be remnants of the precursor composition.

The results of EA (Table 2) showed that WV has a relatively high H/C atomic ratio of 0.41, which indicates a low aromaticity degree. Furthermore, the sum of C, H, N, and ash content amounted to only 87.1 wt%, which evidences that the sample has a high O content. These findings are consistent with the fact that chemical activation with H_3PO_4 is usually carried out up to relatively low temperatures (in the range of 400–550 °C) [28,44,64,87], at which the carbonization process is still at an early stage. Finally, it is worth highlighting that the N content was quite low, 0.2 wt%.

Table 2. Data of mass variation during ammonization (Δm_{am}), PZC, elemental analyses, and titration.

Sample	¹ Δm_{am} (%)	PZC	Elemental Analysis			Titration (mmol g^{-1})		
			C (wt%)	H (wt%)	N (wt%)	² H/C	Acidic	Basic
WV	-	4.7	80.0	2.7	0.2	0.41	1.11	0.45
WVN400	−4.2	6.8	73	2.4	3.9	0.39	0.50	0.38
WVN800	−10.8	6.2	79.0	1.9	5.5	0.29	0.33	0.75
WVC	-	6.2	84.9	1.1	0.2	0.16	0.19	0.32
WVCN400	+3.2	6.1	78.2	1.0	2.8	0.15	0.15	0.43
WVCN800	−1.5	6.3	82.5	1.3	3.5	0.19	0.07	0.86
WVAc	-	1.8	80.2	3.2	2.7	0.48	1.94	0.00
WVAcN400	−1.8	3.4	77.4	3.2	6.8	0.50	1.06	0.64
WVAcN800	−32.4	6.9	89.9	1.4	1.6	0.19	0.32	0.68

¹ Mass variation during ammonization, ² atomic ratio.

The survey XPS spectrum of WV is displayed in Figure S1a in Supplementary Materials (SM). The elemental composition (wt%) determined from the high-resolution (HR) XPS spectra was C 83.1; O 13.7; N 0.3; P 1.3; Na 1.3; and Si 0.3 (Table 3). It is worth pointing out that the data regarding phosphorous and metallic elements are in good accordance with the above reported ED-XRF data obtained from ashes analysis. In turn, the C and N contents are relatively well in agreement with the data of EA (Table 2). Considering that XPS is a superficial technique that provides an estimation of the chemical composition of the few uppermost layers of the external surface, while EA and ash analysis by ED-XRF scrutinize the composition of the material as a bulk, it is possible to conclude that WV has a fairly homogeneous chemical composition through the radial direction.

Table 3. Data of surface chemical composition determined by XPS.

Sample	Element Content (wt% $\pm$ 5%)					
	C	O	N	P	Na	Si
WV	83.1	13.7	0.3	1.3	1.3	0.3
WVN400	83.2	10.7	3.1	1.3	1.2	0.5
WVN800	84.9	7.2	5.1	1.2	1.0	0.6
WVC	86.2	8.4	0.8	2.4	1.6	0.6
WVCN400	85.3	8.1	3.1	1.8	0.7	1.0
WVCN800	85.3	7.6	3.9	1.1	1.1	1.1
WVAc	80.1	17.0	1.7	0.8	-	0.4
WVAcN400	81.4	9.5	7.8	1.0	-	0.3
WVAcN800	89.1	8.3	1.9	0.4	-	0.3

The HR-XPS C 1s core level spectrum of WV was deconvoluted into four components (Figure 5a), which were assigned, in accordance with the literature [88], mainly to unfunc-

tionalized carbons, mostly aromatic carbons (CI peak; 284.8 eV); C–O (CII peak; 286.2 eV); C = O (CIII peak; 287.4 eV); and COO[−] (CIV peak; 288.8 eV). The relative contributions of each peak are reported in Table 4.

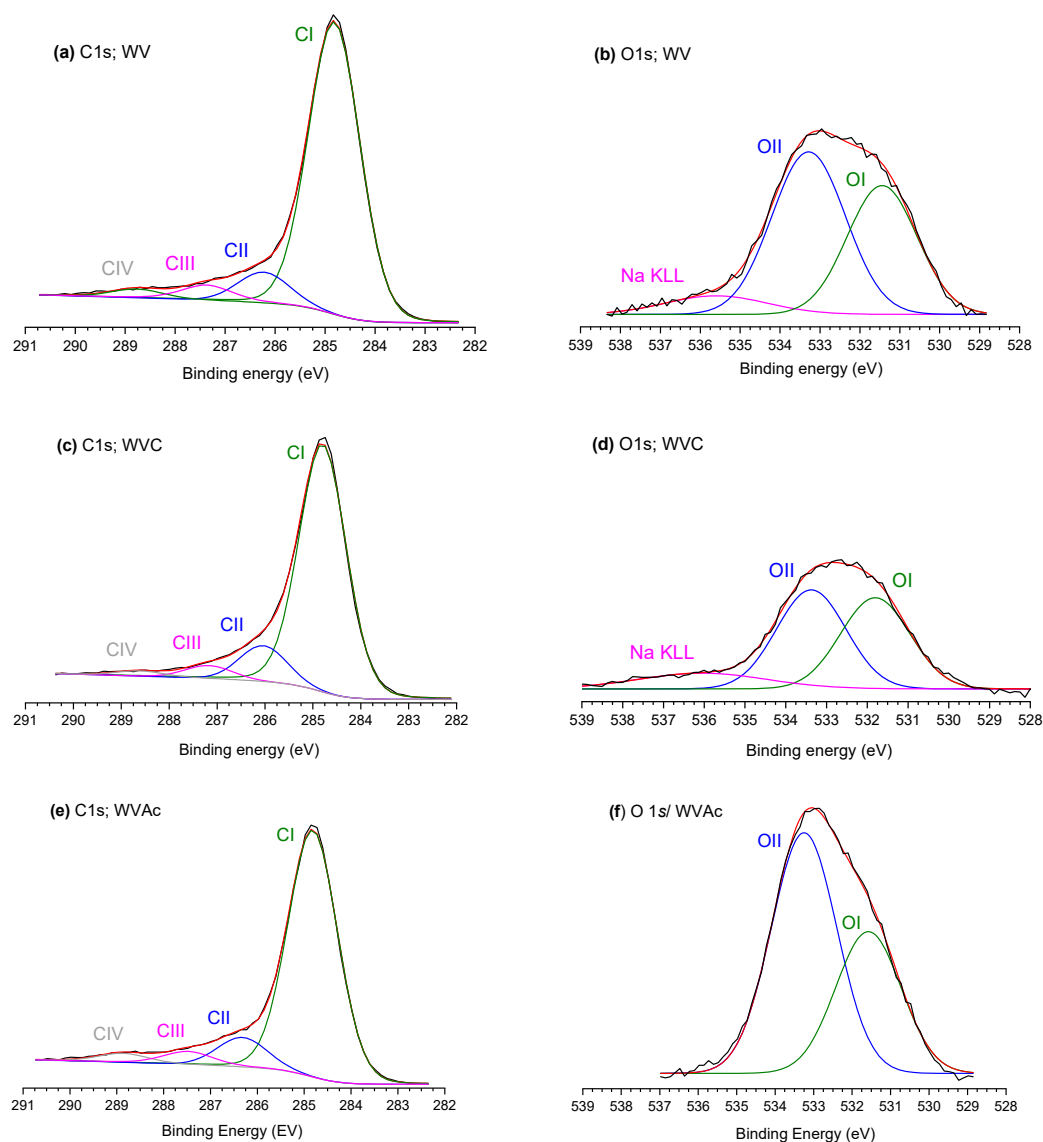


Figure 5. HR-XPS C 1s and O 1s core level spectra.

Table 4. Relative contributions of C 1s and O 1s peaks obtained from the HR-XPS spectra considering each element separately and, between brackets, all the identified elements.

Sample	Relative Contributions (wt% $\pm$ 5%)					
	CI	CII	CIII	CIV	OI	OII
WV	83.7 (69.5)	8.7 (7.2)	4.9 (4.1)	2.7 (2.2)	42.9 (5.8)	57.1 (7.8)
WVN400	82.7 (68.7)	11.3 (9.4)	3.9 (3.3)	2.1 (1.7)	57.5 (6.2)	42.5 (4.6)
WVN800	79.3 (67.3)	13.8 (11.8)	4.8 (4.1)	2.1 (1.8)	46.3 (3.7)	53.7 (3.5)
WVC	82.8 (71.4)	11.4 (9.8)	4.1 (3.5)	1.7 (1.5)	47.9 (4.0)	52.1 (4.3)
WVCN400	80.8 (68.9)	12.6 (10.7)	4.8 (4.1)	1.8 (1.6)	48.1 (3.9)	51.9 (4.2)
WVCN800	79.8 (68.1)	13.0 (11.1)	5.0 (4.3)	2.2 (1.8)	46.4 (3.5)	53.6 (4.1)
WVAc	82.2 (65.8)	9.7 (7.8)	4.9 (3.9)	3.2 (2.6)	37.0 (6.3)	63.0 (10.7)
WVAcN400	76.3 (62.1)	14.8 (12.0)	6.2 (5.1)	2.7 (2.2)	53.1 (5.0)	46.9 (4.4)
WVAcN800	76.4 (68.0)	15.1 (13.4)	6.4 (5.7)	2.1 (1.9)	10.8 (0.9)	89.2 (7.4)

Concerning the deconvolution of the HR-XPS O 1s core level spectrum of ACs and the assignment of the resulting peaks, the literature brings plenty of conflicting information. The website corresponding to reference [89] displays a compilation of data concerning the assignment of O 1s peaks for a variety of O-containing functionalities, which were taken from the work of Beamson and Briggs [90]. These data were used to elaborate Figure S2 in SM. This figure makes clear that, independent of the functional group, O double bonded to C tends to yield O 1s peaks in the range of around 531–533 eV, while oxygen single bonded to carbon tends to render O 1s peaks at higher BEs, in the range of around 533–534 eV. Therefore, a simplified procedure was adopted in the present work, which consisted of deconvoluting the O 1s envelope into only two peaks assigned to oxygen in C=O (OI peak) and C–O (OII peak) moieties. This procedure has been largely adopted by several authors [42,44,54,60] because it is able to provide relevant information while avoiding doubtful interpretations.

At this point, it is worth mentioning that, for the samples that contain small amounts of Na, a KLL Auger signal of this element was identified at around 535.6 eV (Figure 5b,d). Since this signal partially overlapped the O 1s envelope, it was separated from OI and OII peaks during deconvolution. Through this, the O 1s XPS spectrum of WV gave rise to OI and OII peaks centered at 531.4 and 533.3 eV, respectively (Figure 5b).

In accordance with its high O content and low aromaticity, WV rendered relatively intense CO₂, CO, H₂O, and H₂ emissions during TPD analysis (Figure 6). CO and CO₂-TPD profiles have been widely employed to identify oxygenated functionalities on the surface of carbon-based materials. However, doing the peaks assignments is not such a trivial task and there is contradictory information in the literature, as clearly evidenced by the data compiled by Figueiredo et al. [15] and Herold et al. [91].

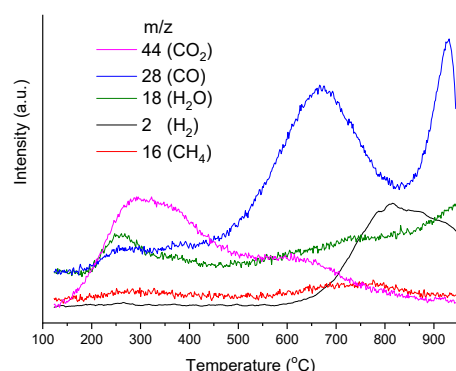


Figure 6. TPD profiles of WV.

In the present work, the CO₂-TPD profile of WV was deconvoluted into five peaks (Figure 7a) whose assignments were conducted according to references [16,92–95]. In this sense, the first two peaks (CO₂-I at 278 °C and CO₂-II at 388 °C) were assigned to the decomposition of stronger and weaker carboxylic acids, respectively. The third peak (CO₂-III at 518 °C) was assigned to carboxylic anhydrides. In turn, the last two peaks (CO₂-IV at 640 °C and CO₂-V at 765 °C) were mainly assigned to lactones (although it is worth mentioning that they can have some contribution from the conversion of CO into CO₂, as will be opportunely discussed in Section 3.4.1).

In turn, the CO-TPD profile was deconvoluted into seven peaks (Figure 7b). The first two (CO-I at 278 °C and CO-II at 388 °C) also correspond to the decomposition of carboxylic acids because, although the decomposition of these groups did not release CO by itself, the fragmentation of CO₂⁺ ions in the ionization chamber of the mass spectrometer generates CO⁺ ions [16]. Furthermore, the possibility cannot be ruled out that CO was also formed inside the sample cell due to the conversion of as-formed CO₂ molecules catalyzed by the

AC surface (Boudouard reaction [96]). The third CO peak (CO-III at 515 °C) was assigned to carboxylic anhydrides, which release both CO₂ and CO simultaneously (therefore, the CO-III and CO₂-III peaks were located at almost the same temperature).

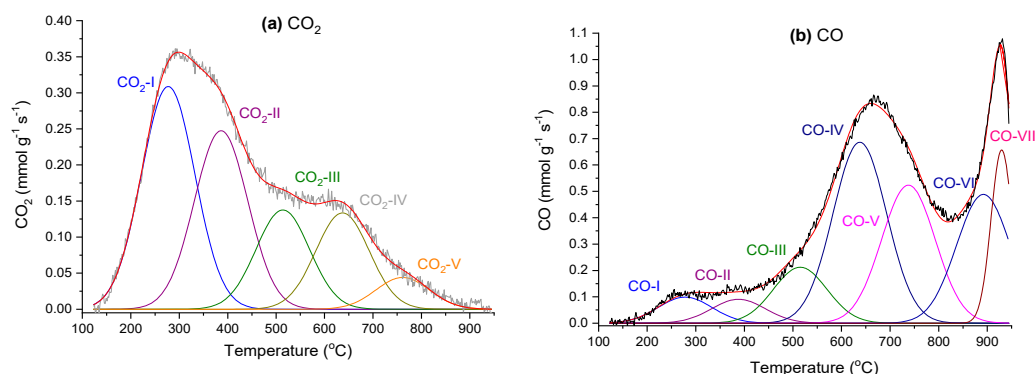


Figure 7. (a) CO₂ and (b) CO-TPD profiles of WV and respective deconvoluted peaks.

Before proceeding with the assignments for the other CO peaks, it is worth highlighting that, while, on the one hand, there is agreement in the literature that the presence of an intense CO emission peak in the ~600–700 °C range is due to the decomposition of phenols/ethers [16,92–95,97], on the other hand, there are controversial proposals for the assignment concerning CO emission in the ~700–800 °C range. For example, Rocha et al. [16] and Li et al. [92] attributed this emission to carbonyl groups in ketone and quinone-like structures. However, Ishii and Ozaki [94], who carried out a detailed work involving TPD analyses of ACs isotopically labeled with deuterium, attributed both the CO peaks observed at 636 and 750 °C to the decomposition of phenol/ether groups, while the emissions due to the decomposition of carbonyl-containing functionalities were assigned to peaks at higher temperatures. In addition, Dungen et al. [97], who achieved a better peak separation by carrying out nonlinear TPD analyses of carbon-based material, concluded that, while phenols and ethers decompose between 620 and 800 °C, carbonyl-containing functions decompose all only above 800 °C.

In the present work, the assignments of the CO peaks were made according to the proposal of the Ishii and Dungen teams. Thus, the peaks verified at 648 and 737 °C (CO-IV and CO-V peaks) in the CO-TPD profile of WV were both assigned to C–O–H/C moieties in phenols/ethers, while the peaks at around 892 and 930 °C (CO-VI and CO-VII) were assigned to carbonyl-containing groups (ketones/quinones). The adoption of this assignment line was supported by the fact that, as will be reported in Section 3.3, the intensity of the CO-V peak increased after nitrification of WV, whereas the peaks above around 800 °C vanished. Therefore, if it is assumed that treatment with HNO₃ increases the number of phenolic groups and oxidizes existing carbonyl groups, then it is possible to infer that the CO-V peak was due to C–O–H/C motifs in phenols/ethers, while the CO-VI and CO-VII peaks were due to carbonyl-containing groups.

In accordance with TPD analyses, the titration of WV resulted in a relatively high content of acidic groups, 1.11 mmol g^{−1}, besides a moderate content of basic groups, 0.45 mmol g^{−1} (Table 2). Accordingly, WV presented a somewhat acidic PZC of 4.7.

3.2. Complementary Carbonization of WV

As already mentioned in the Section 3.1, chemical activation with H₃PO₄ is usually carried out up to relatively low temperatures (usually 400–550 °C) and, therefore, the resulting materials are still in an incipient carbonization degree. Therefore, to achieve a material with higher aromaticity and lower content of acidic oxygenated functional groups, WV was submitted to a complementary carbonization up to 800 °C.

As expected, the treatment gave rise to a considerable weight loss, 12.4%. Since a TPD experiment can be considered as a kind of carbonization in small scale, the reasons for the quoted weight loss can be disclosed taking into account the TPD profiles of WV. In this sense, the majority of the weight loss can be attributed to the release of CO_2 and CO due to the decomposition of oxygenated groups (Figures 6 and 7; see pertinent discussions in Section 3.1). Furthermore, the releases of H_2O , H_2 , and CH_4 (Figure 6) have minor contributions. The release of H_2O in the range of $\sim 200\text{--}320^\circ\text{C}$ is mainly attributed to the occurrence of dehydration reactions involving two neighboring carboxylic acid groups, two phenol groups, or a carboxylic acid and a phenol group [94,95,98]. In turn, the release of H_2 above around 650°C is due to the occurrence of reactions of aromatization and condensation of aromatic rings [94,99]. Finally, the slight release of CH_4 that takes place in the range of $\sim 550\text{--}900^\circ\text{C}$ is due to the presence of some aliphatic carbons.

Concerning the TPD of the sample that underwent complementary carbonization (WVC), one could foresee that it would not give rise to any emissions below 800°C because the material has already been heated up to this temperature. However, although in low intensity, WVC presented some CO_2 and CO emissions below 800°C (Figure 8). The explanation for this behavior is that carbon atoms with incomplete valencies and unpaired electrons are left behind after carbonization, and these atoms are able to react with atmospheric oxygen and water vapor to generate acidic oxygenated groups [100,101]. As would be expected, CO emissions were intensified above 800°C due to the decomposition of carbonyl-containing groups.

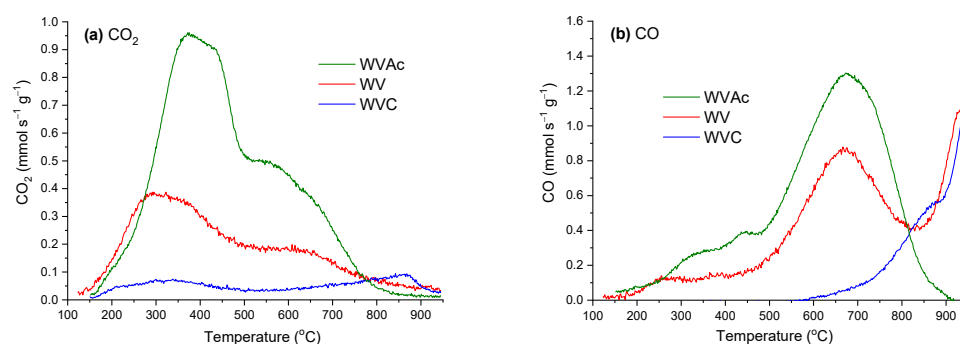


Figure 8. (a) CO_2 and (b) CO -TPD profiles.

In accordance with the above-described reactions that take place during complementary carbonization, WVC presented, in comparison to WV, a lower H/C atomic ratio and O content, which decreased from 0.41 to 0.16 (Table 2) and from 13.6 to 8.4 wt% (Figure S1b in SM; Table 3), respectively. In addition, both the acidic and basic contents decreased: from 1.11 to 0.19 mmol g^{-1} and from 0.45 to 0.32 mmol g^{-1} , respectively (Table 2). Finally, PZC increased from 4.7 to 6.2 (Table 2).

Another important change observed during the complementary carbonization of WV was a reduction in porosity: V_{mic} and V_{mes} decreased from 0.51 and $0.41 \text{ cm}^3 \text{ g}^{-1}$ to 0.44 and $0.31 \text{ cm}^3 \text{ g}^{-1}$, respectively (Table 1). Consequently, SSA also decreased, from 1506 to $1296 \text{ m}^2 \text{ g}^{-1}$. These results can be attributed to the aromatization and condensation of aromatic rings that took place during complementary carbonization, which caused a shrinkage of the material particles and, consequently, a contraction of pore dimensions. Similar results were reported elsewhere for the complementary carbonization of carbons chemically activated with H_3PO_4 and ZnCl_2 [102,103].

3.3. Nitrification

The treatment of WV with HNO_3 promoted a pronounced increase in the acidic content, from 1.11 to 1.94 mmol g^{-1} , whereas the content of basic groups became zero (Table 2). Accordingly, PZC pronouncedly decreased from 4.7 to 1.8.

Concerning the TPD profiles (Figure 8), the intensity of all CO_2 emissions pronouncedly increased after nitrification, which evidenced the creation of additional carboxylic acids, anhydrides, and lactones. In turn, CO emissions intensified up to $\sim 830^\circ\text{C}$ due to the creation of additional anhydride and phenol groups. An interesting aspect to be noted is that CO emissions at higher temperatures (above $\sim 830^\circ\text{C}$) vanished after nitrification, which is in accordance with the null content of basic groups measured by titration for WVAc (Table 2). The consumption of carbonyl groups can be attributed to the oxidative attack of HNO_3 , a well-known reaction [104].

The HNO_3 treatment increased the O content (determined by XPS) from 13.6 to 17.0 wt% (Figure S1c in SM; Table 3). Furthermore, there was an increase in the N content, from 0.2/0.3 to 2.7/1.7 wt% (EA (Table 2)/XPS (Table 3)). The HR-XPS N 1s core level spectrum (Figure 9) reveals that N was inserted as nitro groups ($-\text{NO}_2$), leading to a peak centered at 406 eV [18,64,72,87]. Finally, the Na present in the pristine AC WC was leached by the employed HNO_3 solution (Table 3).

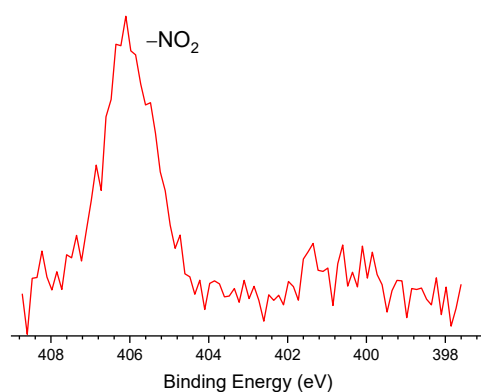


Figure 9. HR-XPS N 1s core level spectrum for the AC modified by nitrification (WVAc).

Figure 4 and Table 1 portray that nitrification somewhat reduced the available porosity and SSA. This is a typical behavior commonly attributed to two factors: (i) the formation of acidic oxygenated groups that can block the entrance of some narrow pores and (ii) the collapse of some pore walls by oxidation [98,105]. In the present case, since nitrification was conducted under mild conditions (dilute HNO_3), we believe that the first reason was preponderant.

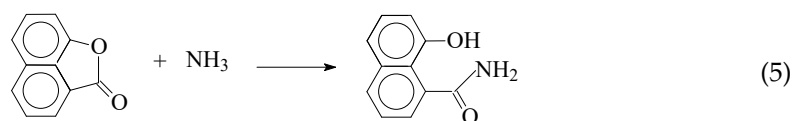
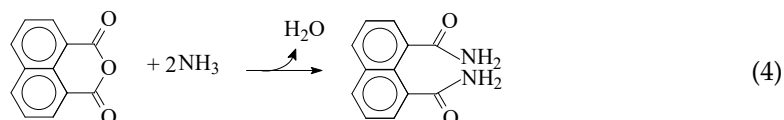
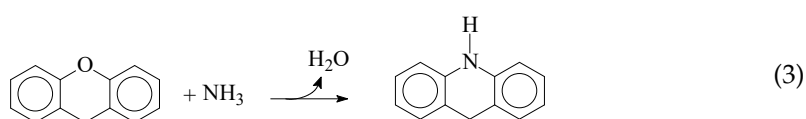
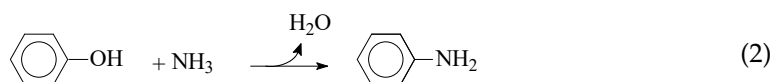
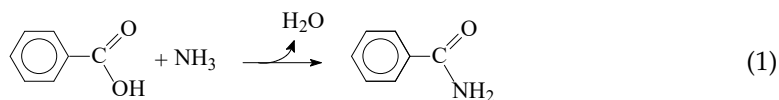
3.4. Ammonization

The results of EA (Table 2) and XPS (Figure S3 in SM; Table 3) show that ammonization up to both 400 and 800°C promoted the desired nitrogen incorporation. It is notable that there is a relatively good agreement between the N content determined through the different analytical methods. Considering that, as already mentioned in Section 3.1, XPS is a surface technique while EA is a bulk technique, these results can be taken as evidence that NH_3 diffused well throughout the carbon particles.

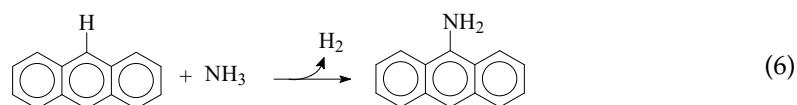
3.4.1. Ammonization up to 400°C

Among the materials prepared by ammonization up to 400°C , WVAcN400 presented the highest N content, 6.8/7.8 wt% (EA (Table 2)/XPS (Table 3)). This material was produced from WVAc, the sample that had been pretreated with HNO_3 and, therefore, had the

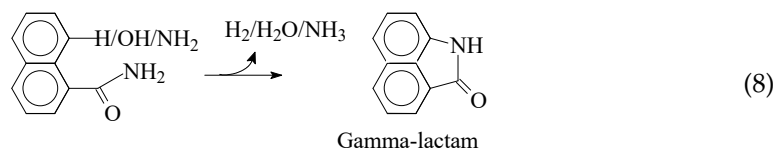
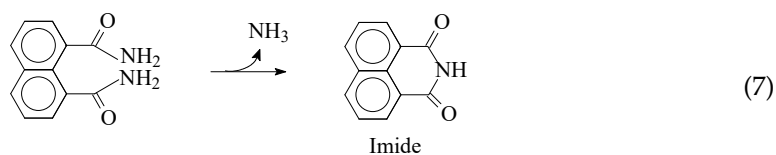
highest content of oxygenated acidic groups among the materials submitted to ammonization. These findings suggest that N incorporation is favored by the presence of oxygenated acidic groups on the surface of the starting material. Indeed, Stohr et al. [106] proposed that, under heating, NH_3 reacts with carboxylic acid and phenol/ether groups to render amides and amines, respectively, as represented in Equations (1)–(3). Furthermore, Ortega et al. [80] proposed that other carboxylic groups such as anhydrides and lactones also react with NH_3 , as illustrated by Equations (4) and (5).

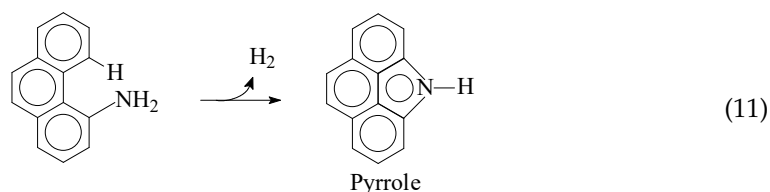
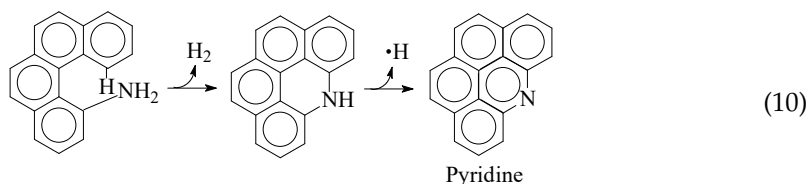
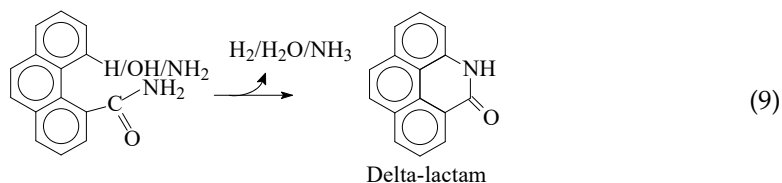


At this point, it is worth noting that WVCN400 presented considerable N content, 2.8/3.1 wt% (EA (Table 2)/XPS (Table 3)), despite the low presence of oxygenated acidic groups in the starting material (WVC). This result evidences that there must exist another pathway for N incorporation that does not depend on the presence of oxygenated acidic groups. We speculate that a temperature of 400 °C is high enough to promote the insertion of $-\text{NH}_2$ groups (aminic nitrogen) directly onto the edge carbon atoms, as illustrated by Equation (6).



In the sequence, the amides and amines formed as illustrated in Equations (1)–(6) would undergo a series of cyclization reactions, as shown in Equations (7)–(11), some of which have already been suggested by other authors [80,83].





Some additional reactions have also been described. For example, Arrigo et al. [18], Ortega et al. [80], and Kundu et al. [81] proposed the decarbonilation of delta-lactams into pyrrole (Equation (12)). Furthermore, Arrigo et al. [18] proposed that the iminol tautomeric form of amides could lose H₂O to form pyridine (Equation (13)). Both reactions are plausible, but we do not have tools to prove their occurrence.

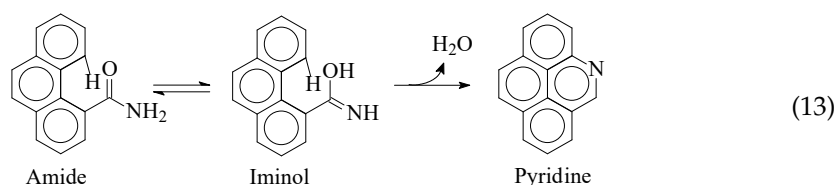
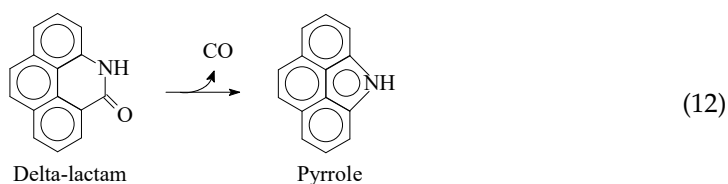
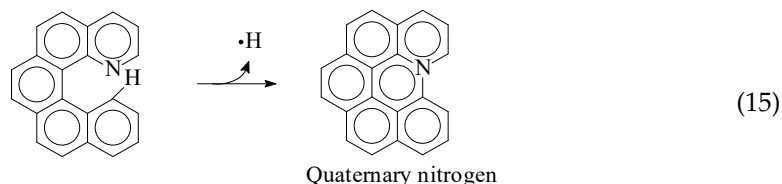
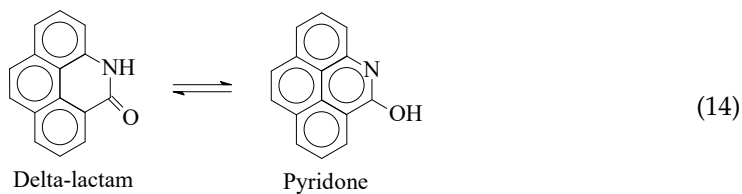


Figure 10a,c,e show the HR-XPS N 1s core level spectra of the samples ammonized up to 400 °C, which present an envelope between around 397 and 402 eV. In accordance with the literature and the above-proposed reactions, this envelope was deconvoluted into four contributions centered at around 398.5, 399.5, 400.3, and 401.5 eV. They were assigned, respectively, mainly to pyridinic N (N-6 peak); aliphatic N (N-X peak) in amines, imides, and lactams; pyrrolic N (N-5 peak); quaternary nitrogen (N-Q peak) [21,25,28,45,51,56,57,64,66,68,79,82]. Furthermore, some authors [14,52,79] have considered that the peak at around 400.3 eV (that is to say, N-5, according to the employed nomenclature) can also have a contribution from pyridone-like structures, which are formed as tautomeric forms of delta-lactams (Equation (14)). The presence of some N-Q could be explained by the occurrence of reactions such as that displayed by Equation (15).



It is worth pointing out that the -NO_2 groups previously introduced by the nitrification treatment were completely removed during ammonization, as revealed by the absence of a peak between 404 and 408 eV in the HR-XPS N 1s core level spectrum of WVAcN400 (Figure 10e).

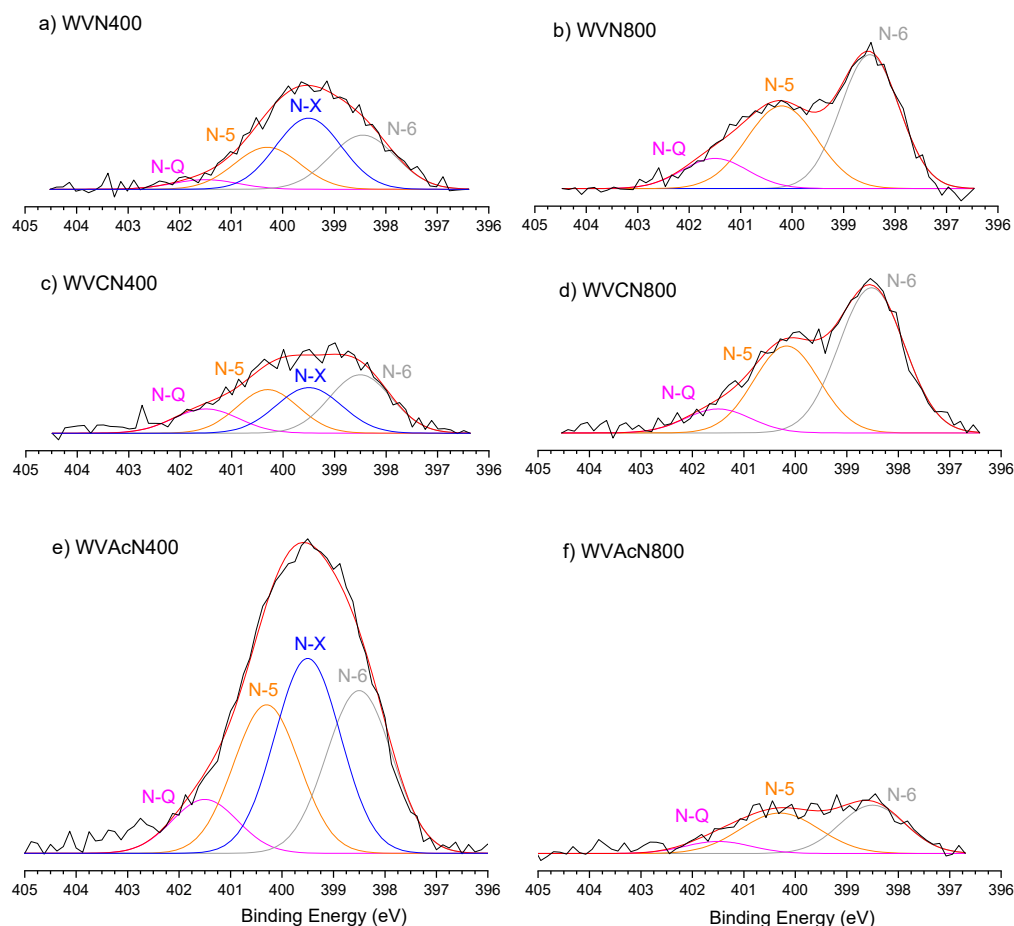


Figure 10. HR-XPS N 1s core level spectra for the ammonized ACs.

Mass losses of 4.2 and 1.8% took place during the ammonization procedures leading to WVN400 and WVAcN400, respectively, while a mass gain of 3.2% occurred during the ammonization that produced WVCN400 (Table 2). These results are in accordance with the idea that, for materials with a relatively high content of oxygenated acidic groups, N incorporation takes place primarily through the reactions described by Equations (1)–(5), followed by reactions like those in Equations (7)–(9), (12) and (13). In general terms, these

reactions release small molecules such as NH_3 , CO , and H_2O , which would explain the slight weight loss observed during the ammonization of WV and WVAc up to 400°C . On the other hand, in the case of samples with low content of oxygenated acidic groups, the initial incorporation of N would take place mainly through reactions like that presented by Equation (6), followed by reactions like those illustrated by Equations (10), (11) and (15). The combination of these reactions would explain the small mass gain verified during the ammonization of WVC up to 400°C .

In accordance with the proposed reactions, N incorporation during ammonization up to 400°C was followed by reductions in O content: from 13.6 (WV) to 10.7 wt% (WVN400); from 8.4 (WVC) to 8.1 wt% (WVCN400); and from 17.0 (WVAc) to 9.5 wt% (WVAc400) (Table 3). In the case of WVC, the reduction was slight because, as discussed above, the main route for N incorporation did not involve the consumption of oxygenated groups. In turn, since WVAc presented, among the samples submitted to ammonization, the higher content of oxygenated groups, it underwent the largest reduction in O content.

As expected, the ammonization up to 400°C of the materials with relatively high content of oxygenated acidic groups increased PZC: from 4.7 (WV) to 6.8 (WVN400) and from 1.8 (WVAc) to 3.4 (WVAcN400) (Table 2). On the other hand, in the case of the material that did not display elevated content of oxygenated acidic groups, WVC, its PZC near the neutrality (6.2) was not significantly altered (the PZC for WVC400 was 6.1).

Figure 11a–c show the CO_2 - and CO -TPD profiles of the samples ammonized up to 400°C . It is notable that the CO profiles were very similar to those of the corresponding materials before ammonization (Figure 8b). In this sense, the presence of an intense peak in the ~ 500 – 850°C region for samples WVN400 and WVAcN400 can be taken as evidence that the conversion of phenol/ether groups into amines according to Equations (2) and (3) was not prominent during ammonization up to 400°C . At this point, it is valid to stress that the remnant of phenolic groups would be able to explain the considerable acidic content verified for the referred samples (0.50 and 1.06 mmol g^{-1} , respectively).

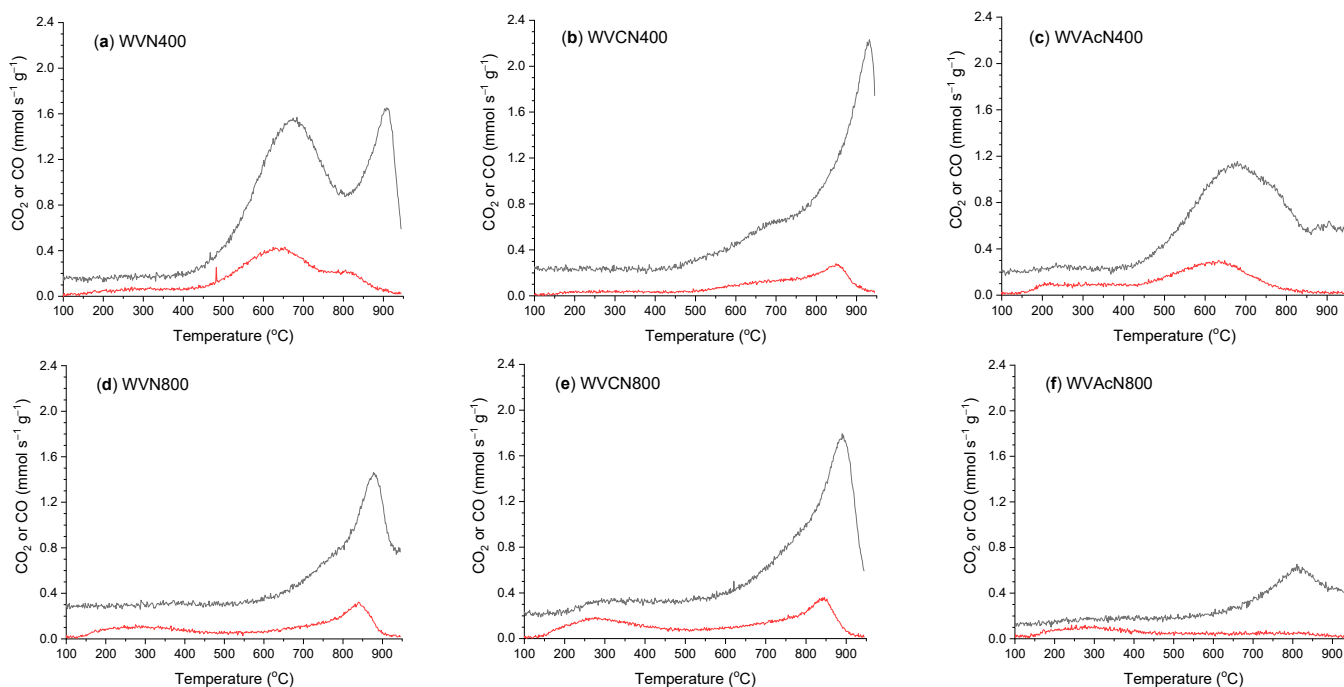
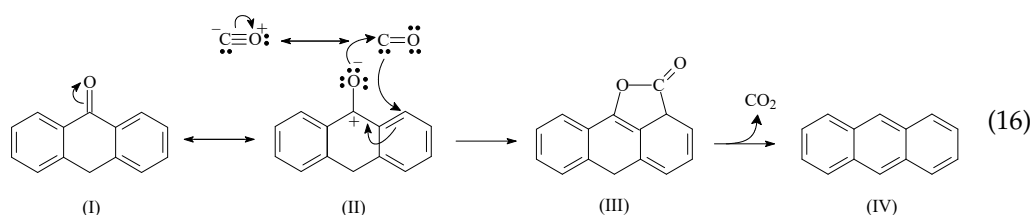


Figure 11. CO_2 - (red lines) and CO -TPD (black lines) profiles of ammonized samples (the scale was kept the same in order to facilitate comparisons).

In turn, the CO₂-TPD profile was completely modified by ammonization up to 400 °C. Below ~450 °C, CO₂ emissions practically disappeared because, as discussed above, carboxylic acids reacted with NH₃ or even decomposed. On the other hand, CO₂ release was intensified in the range of ~500–900 °C, which is somewhat surprising because, as already discussed in Section 3.1, as a rule, CO₂ is released only by the decomposition of carboxylic groups in the low to medium temperature range. An interesting aspect to be noted is that the CO₂-TPD profiles of the samples ammonized up to 400 °C seem to correlate with the corresponding CO profiles in the medium-to-high temperature range. For example, samples WVN400 and WVAcN400 present large CO₂ emission between around 450 and 800 °C, which resembles the CO emission in this same temperature range. Concerning higher temperatures, it is notable that the samples that released CO above ~800 °C (WVN400 and WVCN400) also released some CO₂ in the ~800–900 °C range, whereas the sample that did not emit CO above ~800 °C (WVAcN400) also did not emit any CO₂. These results strongly suggest that at least most of the CO₂ detected during TPD analyses of ammonized samples would actually be the result of a partial conversion of the released CO to CO₂ within the sample holder (the so-called inverse Boudouard reaction [96]).

At this point, it is worth mentioning that lactones decompose in the range of ~500–900 °C (Figure 7). However, it is assumed that the lactones reacted with NH₃ during ammonization; furthermore, the CO₂ emissions in the range of ~500–900 °C were even more intense for the materials ammonized up to 400 °C than for the corresponding materials before ammonization (compare the CO₂-TPD profiles of samples WVN400 and WVAc400 in Figure 11a,c with those of samples WVN and WVAc in Figure 8a). Therefore, it is unlikely that lactone decomposition have significantly contributed to the CO₂ emissions verified in the range of ~500–900 °C in the TPD profiles of the ACs ammonized up to 400 °C.

Marchon et al. [107] proposed that the conversion of CO to CO₂ involves the reaction of a carbonyl group with CO to give a lactone, which would decompose in the sequence to release CO₂. A possible mechanism to explain this reaction is proposed in Equation (16). Since the conversion of CO into CO₂ was significantly observed only for ammonized samples, it is possible to infer that the referred conversion is favored by the presence of N-containing groups. This hypothesis is in accordance with the proposed mechanism since, as portrayed in Figure 2, N-containing groups increase the density of π electrons on the carbon basal planes, which would increase the contribution of the resonant structure (II) in Equation (16) to the overall hybrid structure and, therefore, would favor the nucleophilic attack of carbonylic oxygens to CO.



An additional point that is worth addressing here is that the relative intensity between CO₂ emission and the corresponding CO emission became lower the higher the temperature. Thus, for example, while CO emissions for WVN400 had two well-defined intense maxima around 675 and 910 °C, the corresponding CO₂ emissions presented a maximum at 640 °C with a kind of elbow at ~810 °C (Figure 11a). This behavior can be understood in light of the mechanism proposed above for the conversion of CO into CO₂: firstly, because the nitrogenated groups, which would favor the conversion, gradually decompose as the temperature increases, which would contribute to decrease the rate of CO conversion into CO₂; secondly, because the carbonyl groups that promote the conversion start to decompose

above ~ 800 °C (remember that the CO to be converted at higher temperatures is formed precisely by the decomposition of carbonyls).

Figure 12 and the data in Table 1 show that the ammonization of WV and WVAc up to 400 °C reduced the porosity, while it changed little in the case of ammonization of the sample that had previously been submitted to complementary carbonization (WVC).

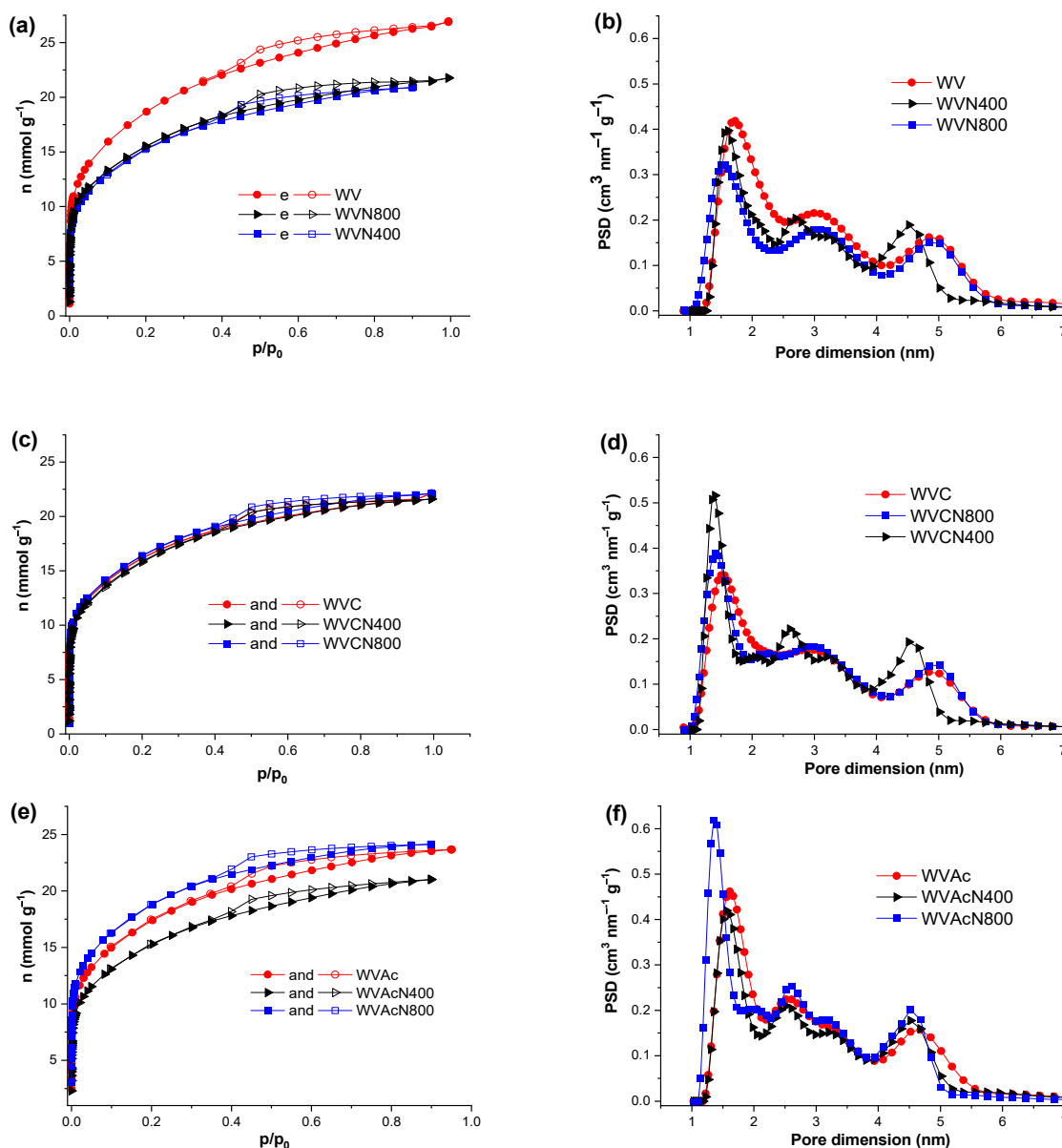


Figure 12. (a,c,e) N_2 adsorption–desorption isotherms of the ammonized samples and (b,d,f) the corresponding PSD curves (for the sake of comparison, the isotherms and PSD curves of the respective starting materials were included; closed and open symbols correspond to the adsorption and desorption branches, respectively).

3.4.2. Ammonization up to 800 °C

Increasing the maximum ammonization temperature from 400 to 800 °C caused different effects on N incorporation depending on the chemical composition of the starting material. For the unmodified AC (WV) and the sample that had previously been submitted to complementary carbonization (WVC), the N incorporation during ammonization up to 800 °C was higher than during ammonization up to 400 °C. The N contents were 5.5/5.1 and 3.5/3.9 wt% for WVN800 and WVCN800, respectively, whereas the values for their

counterparts ammonized up to 400 °C were 3.9/3.1 and 2.8/31 (EA (Table 2)/XPS (Table 3)). Additional incorporation of nitrogen above 400 °C is assumed to occur due to the reaction of NH_3 (or derived species such as $\cdot\text{NH}_2$ radical) with the edge carbons in a manner similar to that illustrated by Equation (6).

On the other hand, for the sample that had been previously treated with HNO_3 (WVAc), the effect of increasing the ammonization temperature was contrary, so that WVAcN800 presented a much lower N content than WVAcN400 (the values were 1.6/1.9 and 7.8/6.8 wt%, respectively; EA (Table 2)/XPS (Table 3)). These results can be related to the intense weight loss verified during the ammonization of WVAc up to 800 °C, 32.4% (Table 2), and shows that, if, on the one hand, the presence of oxygenated acidic groups favors N incorporation at low-to-medium temperatures, on the other hand, the resulting structure is highly susceptible to decomposition at higher temperatures, which leads to the release of most of the N incorporated at lower temperatures. For the sake of comparison, the weight losses during the ammonization of WV and WVC up to 800 °C were 10.8 and 1.5%, respectively.

The HR-XPS N 1s core level spectra of the samples ammonized up to 800 °C presented different profiles than those verified for their counterparts ammonized up to 400 °C (compare Figure 10b with Figure 10a, Figure 10d with Figure 10c, and Figure 10f with Figure 10e). The N-X peak due to aliphatic N, prominent for the samples ammonized up to 400 °C, was not present in the spectra of the samples ammonized up to 800 °C. For the latter, only aromatic N, mainly pyrrolic (N-5) and pyridinic (N-6), is present. At this point it is worth highlighting that a similar trend can be observed in the N 1s core level spectra of the materials prepared through ammonization up to different temperatures by other authors [18,45,69,81]. In this sense, Arrigo et al. [18] reported N-X contents (called, in their work, N2 peak) of 5.0, 6.7, and 0.0 for materials obtained by ammonization up to 200, 400, and 600 °C, respectively, of a carbon nanofiber pretreated with HNO_3 (concentrated, 120 °C, 2 h).

As expected, the TPDs of the samples ammonized up to 800 °C (Figure 11d–f) presented low CO and CO_2 emission up to this temperature. Similar to the material submitted to complementary carbonization (Section 3.2), the minor emissions that took place below the maximum temperature reached during the material processing are attributed to functional groups formed by post-synthesis reaction with atmospheric O_2 and H_2O . In turn, the intense CO emission peak verified for WVN800 and WVCN800 at around 880–890 °C is assigned to the decomposition of carbonyl groups. In the case of WVAcN800, this emission is not observed because, as already discussed in Section 3.3, the carbonyl groups were consumed by the pretreatment with HNO_3 . It is noteworthy that, in the same way as verified for the samples ammonized up to 400 °C, the CO emissions from the samples ammonized up to 800 °C had a corresponding less intense evolution of CO_2 , supposedly due to the conversion of CO into CO_2 (see pertinent discussion in Section 3.4.1).

The samples ammonized up to 800 °C presented a lower O content than the corresponding starting materials and counterparts ammonized up to 400 °C. The values were 13.7/10.7/7.2 wt% for WV/WVN400/WVN800, 8.4/8.1/7.6 wt% for WVC/WVCN400/WVCN800, and 17.0/9.5/8.2 wt% for WVAc/WVAcN400/WVAcN800 (Table 3). In the case of the series WVC/WVCN400/WVCN800, the reduction was slight because WVC had already lost the labile oxygenated groups during the previous complementary carbonization. Furthermore, WVN800 and WVAcN800 had considerably higher aromaticity due to the thermal effects during ammonization. The H/C ratios were 0.41/0.39/0.29 for WV/WVN400/WVN800 and 0.48/0.50/0.19 for WVAc/WVAcN400/WVAcN800 (Table 2). In the case of WVC, as it had already been treated at 800 °C during complementary

carbonization, no additional gain of aromaticity was detected after ammonization (the determined H/C ratios were 0.16/0.15/0.19 for WVC/WVCN400/WVCN800).

As expected, the materials ammonized up to 800 °C presented a higher content of basic groups than acidic groups; the acidic/basic contents were 0.33/0.75, 0.07/0.86, and 0.32/0.68 mmol g⁻¹ for WVN800, WVCN800, and WVAcN800, respectively (Table 2). Though, the corresponding measured PZC values were always near neutrality: 6.2, 6.3, and 6.9.

Concerning the textural properties, it is first necessary to stress that, for materials that have not been previously processed at high temperatures (the cases of WV and WVAc), it would be expected that the increase in the maximum ammonization temperature from 400 to 800 °C would have provoked a porosity shrinkage due to thermal effects, in a similar way as verified when WV was submitted to complementary carbonization (Section 3.2). However, this behavior was not observed in the present study (Figure 12; Table 1). Instead, in the case of sample WVN800, the porosity was much similar to that of its counterpart ammonized up to 400 °C (WVN400). In turn, the porosity of WVAcN800 was much higher than that of its counterpart sample ammonized up to 400 °C (WVAcN400). These findings evidence that another effect balanced or even surpassed the trend of porosity shrinkage due to thermal issues. This effect is supposed to be the above-mentioned degradation, in the medium-to-high temperature range, of labile aliphatic N-containing functionalities formed at lower temperatures. As reported at the end of Section 3.4.1, these functionalities would reduce the available porosity of the sample ammonized up to 400 °C so that their removal would work as a kind of “material gasification” that contributes to increase the available porosity.

As expected, none of the above reported effects were relevant in the case of the WVC ammonization. Firstly, because this material had already been previously processed at high temperature during the complementary carbonization, so that the thermal effect of porosity shrinkage had already taken place (see Section 3.2). Secondly because, since WVC had a low content of oxygenated acidic groups, the formation of labile aliphatic N-containing functionalities was not significant during its ammonization (see pertinent discussions in Section 3.4.1). Therefore, sample WVCN800 had a very similar porosity to its counterpart ammonized up to 400 °C (WVCN400).

3.4.3. Final Considerations About Ammonization

Although there are scarce works in the literature concerning the ammonization of carbon-based materials at (or up to) different temperatures, the results of the existing works are in consonance with those presented here. These works can be divided into two groups. The first group corresponds to the works whose authors carried out the direct ammonization of carbon materials, that is to say, without performing an oxidative pretreatment [30,32,45]. For these authors, the content of N incorporated at higher temperatures was higher, in a similar manner as verified for the ammonization of WV and WVC in the present work. For example, Pevida et al. [30] reported N contents (EA) of 3.3 and 6.3 wt% for the materials obtained through ammonization at 400 and 800 °C (2 h), respectively, of a commercial H₃PO₄ activated carbon; Yang et al. [45] reported N contents (XPS) of 1.03 and 2.80 wt% for the materials obtained through ammonization of a commercial AC up to 350 and 850 °C (2 h), respectively. In the other group are the works whose authors carried out a pretreatment of the carbon material with HNO₃ before ammonization [18,69,80,81]. For these authors, the content of N incorporated at higher temperatures was lower, in a similar manner as verified for the ammonization of WVAc in the present work. For example, Zhang et al. [69] reported N contents (EA) of 4.0 and 2.1 wt% for the materials obtained through ammonization at 400 and 800 °C (2 h), respectively, of the materials obtained through

chemical activation of a petroleum coke with KOH followed by pretreatment with a HNO₃ solution (20 wt%, 3 h, 60 °C); Kundu et al. [81] reported N contents (XPS) of 3.5 and 1.1 wt% for the materials obtained through ammonization at 400 and 800 °C (2 h), respectively, of materials obtained through pretreatment of commercial carbon nanotubes with HNO₃ vapor (48 h, 200 °C).

It is worth mentioning that some authors have inadvertently carried out an oxidative pretreatment with HNO₃ prior to ammonization [18,43,69,80,81], based on the premise that this pretreatment would increase N incorporation. However, the results and discussions reported in the present work show that the effects of pretreating a carbon-based material on the N incorporation depend on the ammonization temperature and the surface chemical composition of the starting material. Therefore, the pertinence of carrying out a nitrification or other oxidative pretreatment should be evaluated on a case-by-case basis.

4. Conclusions

The present work provides valuable insights on the preparation of N-doped ACs through ammonization. The results showed that, during ammonization up to relatively low temperatures (around 400 °C), nitrogen is incorporated in the form of aliphatic (supposedly amines, imides, and lactams), pyridinic, and pyrrolic groups, with a minor contribution of quaternary nitrogen. The presence of oxygenated acidic groups (mainly carboxylic acids, anhydrides, and lactones) on the surface of the starting material favors N insertion by means of the formation of amides that, in the sequence, undergo cyclization reactions to give rise mainly to imides and lactams. Therefore, the highest N content on the AC surface (around 8 wt%, as determined by XPS) was verified for the sample obtained from ammonization up to 400 °C of the material that had been pretreated with a HNO₃ solution (because this pretreatment greatly increased the content of the referred oxygenated acidic groups).

Although the presence of oxygenated acidic groups favors N incorporation, it is not an indispensable requisite because NH₃ can alternatively react directly with edge carbon atoms, presumably to give rise to amine groups that can react in the sequence to form mainly pyridine and pyrrole-like structures. Therefore, even the sample that had been submitted to a previous complementary carbonization up to 800 °C, which presented a quite low content of oxygenated acidic groups, incorporated considerable content of N during ammonization up to 400 °C (around 3 wt%, as determined by XPS).

By increasing the maximum ammonization temperature to 800 °C, two effects were observed: (i) on the one hand, the incorporation of N was favored; (ii) on the other hand, higher temperatures provoked the decomposition of aliphatic groups, which caused the release of part of the N that had been incorporated at lower temperatures. The overall result was that the N present in the materials obtained by ammonization up to 800 °C was found only in the form of aromatic N, mainly pyridinic and pyrrolic ones, with a minor contribution of quaternary N. Furthermore, if the starting material had a high content of oxygenated acidic groups, the N content of the material obtained after ammonization up to 800 °C was lower than that verified for its counterpart ammonized up to 400 °C because most of the N was incorporated in the form of aliphatic groups that decomposed at higher temperatures. In turn, if the starting material had a low-to-medium content of oxygenated acidic groups, the N content verified for the materials prepared by ammonization up to 800 °C was superior to that verified for their counterpart samples ammonized up to 400 °C because a larger amount of N was incorporated in the form of stable aromatic rings.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/c11010015/s1>, Figure S1: XPS survey spectra of the (a) unmodified AC WV and the samples resulting from its (b) complementary carbonization (WVC) and (c) nitrification (WVAc); Figure S2: Binding Energies of XPS O 1s peaks for different functional

oxygenated groups. (Based on reference [89] of the article); Figure S3: XPS survey spectra of the ammonized samples.

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References

1. Novaes, H.R.; Prauchner, M.J.; Ginoris, Y.P. Cylindrospermopsin adsorption onto activated carbons synthesized from coconut shell: Effect of surface chemical composition on removal efficiency. *Adsorpt. Sci. Technol.* **2024**, *42*, 1–20. [\[CrossRef\]](#)
2. Verma, C.; Quraishi, M.A. (Eds.) *Activated Carbon: Progress and Applications*; The Royal Society of Chemistry: London, UK, 2023.
3. Zhao, C.; Ge, L.; Mai, L.; Li, X.; Chen, S.; Li, Q.; Li, S.; Yao, L.; Wang, Y.; Xu, C. Review on coal-based activated carbon: Preparation, modification, application, regeneration, and perspectives. *Energy Fuels* **2023**, *37*, 11622–11642. [\[CrossRef\]](#)
4. Reza, M.S.; Yun, C.S.; Afroze, S.; Radenahmad, N.; Bakar, M.S.A.; Saidur, R.; Taweekun, J.; Azad, A.K. Preparation of activated carbon from biomass and its' applications in water and gas purification, a review. *Arab J. Basic Appl. Sci.* **2020**, *27*, 208–238. [\[CrossRef\]](#)
5. Kasera, N.; Kolar, P.; Hall, S.G. Nitrogen-doped biochars as adsorbents for mitigation of heavy metals and organics from water: A review. *Biochar* **2022**, *4*, 17. [\[CrossRef\]](#)
6. Snezhkova, E.; Redl, H.; Grillari, J.; Osuchowski, M. Activated carbon for sepsis prevention and intervention: A modern way of utilizing old therapies. *C* **2023**, *9*, 72. [\[CrossRef\]](#)
7. Choi, J.-S.; Lim, S.-H.; Lingamdinne, L.P.; Park, S.-Y.; Koduru, J.R.; Yang, J.-K.; Chang, Y.-Y. Development of ultra-high surface area polyaniline-based activated carbon for the removal of volatile organic compounds from industrial effluents. *Environ. Pollut.* **2023**, *337*, 122594. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Tolkou, A.K.; Maroulas, K.N.; Theologis, D.; Katsoyiannis, I.A.; Kyzas, G.Z. Comparison of modified peels: Natural peels or peels-based activated carbons for the removal of several pollutants found in wastewaters. *C* **2024**, *10*, 22. [\[CrossRef\]](#)
9. Al-Hajri, W.; De Luna, Y.; Bensalah, N. Review on recent applications of nitrogen-doped carbon materials in CO₂ capture and energy conversion and storage. *Energy Technol.* **2022**, *10*, 2200498. [\[CrossRef\]](#)
10. Ferrero, G.A.; Fuertes, A.B.; Sevilla, M.; Titirici, M.-M. Efficient metal-free N-doped mesoporous carbon catalysts for ORR by a template-free approach. *Carbon* **2016**, *106*, 179–187. [\[CrossRef\]](#)
11. Kumar Mishra, R.; Singh, B.; Acharya, B. A Comprehensive review on activated carbon from pyrolysis of lignocellulosic biomass: An application for energy and the environment. *Carbon Resour. Convers.* **2024**, *7*, 100228. [\[CrossRef\]](#)
12. Yang, J.; Fu, L.; Wu, F.; Chen, X.; Wu, C.; Wang, Q. Recent developments in activated carbon catalysts based on pore size regulation in the application of catalytic ozonation. *Catalysts* **2022**, *12*, 1085. [\[CrossRef\]](#)
13. Iwanow, M.; Gärtner, T.; Sieber, V.; König, B. Activated carbon as catalyst support: Precursors, preparation, modification and characterization. *Beilstein J. Org. Chem.* **2020**, *16*, 1188–1202. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Figueiredo, J.L.; Pereira, M.F.R. The role of surface chemistry in catalysis with carbons. *Catal. Today* **2010**, *150*, 2–7. [\[CrossRef\]](#)
15. Figueiredo, J.L.; Pereira, M.F.R.; Freitas, M.M.A.; Orfao, J.J.M. Modification of the surface chemistry of activated carbons. *Carbon* **1999**, *37*, 1379–1389. [\[CrossRef\]](#)

16. Rocha, R.P.; Pereira, M.F.R.; Figueiredo, J.L. Characterisation of the surface chemistry of carbon materials by temperature-programmed desorption: An assessment. *Catal. Today* **2023**, *418*, 114136. [\[CrossRef\]](#)
17. Rocha, R.; Soares, O.; Figueiredo, J.; Pereira, M. Tuning CNT Properties for metal-free environmental catalytic applications. *C* **2016**, *2*, 17. [\[CrossRef\]](#)
18. Arrigo, R.; Hävecker, M.; Wrabetz, S.; Blume, R.; Lerch, M.; McGregor, J.; Parrott, E.P.J.; Zeitler, J.A.; Gladden, L.F.; Knop-Gericke, A.; et al. Tuning the acid/base properties of nanocarbons by functionalization via amination. *J. Am. Chem. Soc.* **2010**, *132*, 9616–9630. [\[CrossRef\]](#)
19. Pietrzak, R. XPS study and physico-chemical properties of nitrogen-enriched microporous activated carbon from high volatile bituminous coal. *Fuel* **2009**, *88*, 1871–1877. [\[CrossRef\]](#)
20. Shafeeyan, M.S.; Daud, W.M.A.W.; Houshmand, A.; Shamiri, A. A review on surface modification of activated carbon for carbon dioxide adsorption. *J. Anal. Appl. Pyrolysis* **2010**, *89*, 143–151. [\[CrossRef\]](#)
21. Rehman, A.; Park, S.-J. Comparative study of activation methods to design nitrogen-doped ultra-microporous carbons as efficient contenders for CO₂ capture. *Chem. Eng. J.* **2018**, *352*, 539–548. [\[CrossRef\]](#)
22. Wang, J.; Senkovska, I.; Oschatz, M.; Lohe, M.R.; Borchardt, L.; Heerwig, A.; Liu, Q.; Kaskel, S. Highly porous nitrogen-doped polyimine-based carbons with adjustable microstructures for CO₂ capture. *J. Mater. Chem. A* **2013**, *1*, 10951–10961. [\[CrossRef\]](#)
23. Staciwa, P.; Sibera, D.; Pelech, I.; Narkiewicz, U.; Moszyński, D. CO₂ adsorption studies on spherical carbon derived from resorcinol-formaldehyde resin and sugars. *J. Environ. Chem. Eng.* **2024**, *12*, 111735. [\[CrossRef\]](#)
24. Li, Y.; Zhang, G.; Wu, C.; Liu, J.; Li, G.; Wang, Y.; Zhao, Y. Novel nitrogen-enriched activated carbon with tunable microporosity from agricultural and plastic waste for CO₂ adsorption. *J. Environ. Chem. Eng.* **2023**, *11*, 111257. [\[CrossRef\]](#)
25. Lee, M.-S.; Park, M.; Kim, H.Y.; Park, S.-J. Effects of microporosity and surface chemistry on separation performances of N-containing pitch-based activated carbons for CO₂/N₂ binary mixture. *Sci. Rep.* **2016**, *6*, 23224. [\[CrossRef\]](#) [\[PubMed\]](#)
26. Bai, J.; Huang, J.; Yu, Q.; Demir, M.; Kilic, M.; Altay, B.N.; Hu, X.; Wang, L. N-doped porous carbon derived from macadamia nut shell for CO₂ adsorption. *Fuel Process. Technol.* **2023**, *249*, 107854. [\[CrossRef\]](#)
27. Spessato, L.; Duarte, V.A.; Fonseca, J.M.; Arroyo, P.A.; Almeida, V.C. Nitrogen-doped activated carbons with high performances for CO₂ adsorption. *J. CO₂ Util.* **2022**, *61*, 102013. [\[CrossRef\]](#)
28. Zhang, S.; Zhou, Q.; Jiang, X.; Yao, L.; Jiang, W.; Xie, R. Preparation and evaluation of nitrogen-tailored hierarchical meso-/microporous activated carbon for CO₂ adsorption. *Environ. Technol.* **2020**, *41*, 3544–3553. [\[CrossRef\]](#)
29. Przepiórski, J.; Skrodzewicz, M.; Morawski, A.W. High temperature ammonia treatment of activated carbon for enhancement of CO₂ adsorption. *Appl. Surf. Sci.* **2004**, *225*, 235–242. [\[CrossRef\]](#)
30. Pevida, C.; Plaza, M.G.; Arias, B.; Feroso, J.; Rubiera, F.; Pis, J.J. Surface Modification of Activated Carbons for CO₂ capture. *Appl. Surf. Sci.* **2008**, *254*, 7165–7172. [\[CrossRef\]](#)
31. Shafeeyan, M.S.; Daud, W.M.A.W.; Houshmand, A.; Arami-Niya, A. Ammonia modification of activated carbon to enhance carbon dioxide adsorption: Effect of pre-oxidation. *Appl. Surf. Sci.* **2011**, *257*, 3936–3942. [\[CrossRef\]](#)
32. Plaza, M.G.; Pevida, C.; Arias, B.; Feroso, J.; Casal, M.D.; Martín, C.F.; Rubiera, F.; Pis, J.J. Development of low-cost biomass-based adsorbents for postcombustion CO₂ capture. *Fuel* **2009**, *88*, 2442–2447. [\[CrossRef\]](#)
33. Plaza, M.G.; Rubiera, F.; Pis, J.J.; Pevida, C. Ammoxidation of carbon materials for CO₂ capture. *Appl. Surf. Sci.* **2010**, *256*, 6843–6849. [\[CrossRef\]](#)
34. Bezerra, D.P.; da Silva, F.W.M.; de Moura, P.A.S.; Sapag, K.; Vieira, R.S.; Rodriguez-Castellon, E.; de Azevedo, D.C.S. Adsorption of CO₂ on Amine-Grafted Activated Carbon. *Adsorpt. Sci. Technol.* **2014**, *32*, 141–151. [\[CrossRef\]](#)
35. Li, T.; An, X.; Fu, D. Review on nitrogen-doped porous carbon materials for CO₂ adsorption and separation: Recent advances and outlook. *Energy Fuels* **2023**, *37*, 8160–8179. [\[CrossRef\]](#)
36. Rashidi, N.A.; Yusup, S. An overview of activated carbons utilization for the post-combustion carbon dioxide capture. *J. CO₂ Util.* **2016**, *13*, 1–16. [\[CrossRef\]](#)
37. Hu, W.; Huang, J.; Wang, J.; Xie, D.; Wang, Z.; Qiao, Y.; Xu, M. Benign-by-design N-doped activated carbon from wasted aqueous assisted hydrochar of leftover rice for efficient H₂S removal. *Fuel* **2024**, *358*, 130233. [\[CrossRef\]](#)
38. Bagreev, A.; Angel Menendez, J.; Dukhno, I.; Tarasenko, Y.; Bandoz, T.J. Bituminous coal-based activated carbons modified with nitrogen as adsorbents of hydrogen sulfide. *Carbon* **2004**, *42*, 469–476. [\[CrossRef\]](#)
39. Chu, B.; Amano, Y.; Machida, M. Preparation of bean dreg derived N-doped activated carbon with high adsorption for Cr(VI). *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *586*, 124262. [\[CrossRef\]](#)
40. Yuan, X.; An, N.; Zhu, Z.; Sun, H.; Zheng, J.; Jia, M.; Lu, C.; Zhang, W.; Liu, N. Hierarchically porous nitrogen-doped carbon materials as efficient adsorbents for removal of heavy metal ions. *Process Saf. Environ. Prot.* **2018**, *119*, 320–329. [\[CrossRef\]](#)
41. Guo, S.; Wang, Y.; Wei, X.; Gao, Y.; Xiao, B.; Yang, Y. Structural analysis and heavy metal adsorption of N-doped biochar from hydrothermal carbonization of *Camellia sinensis* Waste. *Environ. Sci. Pollut. Res.* **2020**, *27*, 18866–18874. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Bakry, A.M.; Awad, F.S.; Bobb, J.A.; El-Shall, M.S. Multifunctional binding sites on nitrogen-doped carboxylated porous carbon for highly efficient adsorption of Pb(II), Hg(II), and Cr(VI) ions. *ACS Omega* **2020**, *5*, 33090–33100. [\[CrossRef\]](#) [\[PubMed\]](#)

43. Kasnejad, M.H.; Esfandiari, A.; Kaghazchi, T.; Asasian, N. Effect of pre-oxidation for introduction of nitrogen containing functional groups into the structure of activated carbons and its influence on Cu (II) adsorption. *J. Taiwan Inst. Chem. Eng.* **2012**, *43*, 736–740. [\[CrossRef\]](#)
44. Smith, V.A.; Rivera, J.F.A.; Bello, R.; Rodríguez-Aguado, E.; Elshaer, M.R.; Wodzinski, R.L.; Bashkova, S. The role of surface chemistry and polyethylenimine grafting in the removal of Cr (VI) by activated carbons from cashew nut shells. *C* **2021**, *7*, 27. [\[CrossRef\]](#)
45. Yang, G.; Chen, H.; Qin, H.; Feng, Y. Amination of activated carbon for enhancing phenol adsorption: Effect of nitrogen-containing functional groups. *Appl. Surf. Sci.* **2014**, *293*, 299–305. [\[CrossRef\]](#)
46. Xie, Y.; Hu, W.; Wang, X.; Tong, W.; Li, P.; Zhou, H.; Wang, Y.; Zhang, Y. Molten salt induced nitrogen-doped biochar nanosheets as highly efficient peroxymonosulfate catalyst for organic pollutant degradation. *Environ. Pollut.* **2020**, *260*, 114053. [\[CrossRef\]](#)
47. Liu, X.; Zhangsun, G.; Zheng, Y.; Liang, S.; Cao, Y.; Liu, F.; Xiao, Y.; Jiang, L. Hierarchical N-doped carbons endowed with structural base sites toward highly selective adsorption and catalytic oxidation of H₂S. *Ind. Eng. Chem. Res.* **2021**, *60*, 2101–2111. [\[CrossRef\]](#)
48. Rong, S.; Zhang, L.; Yue, Z.; Song, Z.; Tang, W.; Zhu, X.; Wang, T.; Zhou, X.; Cheng, S.; Xia, X. Directional introduction of pyridine nitrogen functional groups in activated carbon catalysts for the catalytic production of hydrogen: An experimental and DFT Calculation. *Chem. Eng. J.* **2023**, *453*, 139744. [\[CrossRef\]](#)
49. Li, M.; Xu, F.; Li, H.; Wang, Y. Nitrogen-doped porous carbon materials: Promising catalysts or catalyst supports for heterogeneous hydrogenation and oxidation. *Catal. Sci. Technol.* **2016**, *6*, 3670–3693. [\[CrossRef\]](#)
50. Kundu, S.; Nagaiah, T.C.; Xia, W.; Wang, Y.; Van Dommele, S.; Bitter, J.H.; Santa, M.; Grundmeier, G.; Bron, M.; Schuhmann, W.; et al. Electrocatalytic activity and stability of nitrogen-containing carbon nanotubes in the oxygen reduction reaction. *J. Phys. Chem. C* **2009**, *113*, 14302–14310. [\[CrossRef\]](#)
51. Li, O.L.; Chiba, S.; Wada, Y.; Panomsuwan, G.; Ishizaki, T. Synthesis of graphitic-N and amino-N in nitrogen-doped carbon via a solution plasma process and exploration of their synergic effect for advanced oxygen reduction reaction. *J. Mater. Chem. A* **2017**, *5*, 2073–2082. [\[CrossRef\]](#)
52. Quílez-Bermejo, J.; Pérez-Rodríguez, S.; Canevesi, R.; Torres, D.; Morallón, E.; Cazorla-Amorós, D.; Celzard, A.; Fierro, V. Easy enrichment of graphitic nitrogen to prepare highly catalytic carbons for oxygen reduction reaction. *Carbon* **2022**, *196*, 708–717. [\[CrossRef\]](#)
53. Quílez-Bermejo, J.; Pérez-Rodríguez, S.; Torres, D.; Canevesi, R.; Morallón, E.; Cazorla-Amorós, D.; Celzard, A.; Fierro, V. Nitrogen sites prevail over textural properties in N-doped carbons for the oxygen reduction reaction. *J. Colloid Interface Sci.* **2024**, *654*, 446–453. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Barrera, D.; Florent, M.; Sapag, K.; Bandosz, T.J. Insight into the mechanism of oxygen reduction reaction on micro/mesoporous carbons: Ultramicropores versus nitrogen-containing catalytic centers in ordered pore structure. *ACS Appl. Energy Mater.* **2019**, *2*, 7412–7424. [\[CrossRef\]](#)
55. Wang, Y.; Zuo, S.; Liu, Y. Ammonia modification of high-surface-area activated carbons as metal-free electrocatalysts for oxygen reduction reaction. *Electrochim. Acta* **2018**, *263*, 465–473. [\[CrossRef\]](#)
56. Wu, K.; Wang, D.; Su, D.; Gentle, I.R. A Discussion on the activity origin in metal-free nitrogen-doped carbons for oxygen reduction reaction and their mechanisms. *ChemSusChem* **2015**, *8*, 2772–2788. [\[CrossRef\]](#)
57. Wu, B.; Meng, H.; Morales, D.M.; Zeng, F.; Zhu, J.; Wang, B.; Risch, M.; Xu, Z.J.; Petit, T. Nitrogen-rich carbonaceous materials for advanced oxygen electrocatalysis: Synthesis, characterization, and activity of nitrogen sites. *Adv. Funct. Mater.* **2022**, *32*, 2204137. [\[CrossRef\]](#)
58. Li, S.; Xu, R.; Wang, H.; Brett, D.J.L.; Ji, S.; Pollet, B.G.; Wang, R. Ultra-high surface area and mesoporous N-doped carbon derived from sheep bones with high electrocatalytic performance toward the oxygen reduction reaction. *J. Solid State Electrochem.* **2017**, *21*, 2947–2954. [\[CrossRef\]](#)
59. Zhang, Z.; Yu, L.; Tu, Y.; Chen, R.; Wu, L.; Zhu, J.; Deng, D. Unveiling the active site of metal-free nitrogen-doped carbon for electrocatalytic carbon dioxide reduction. *Cell Rep. Phys. Sci.* **2020**, *1*, 100145. [\[CrossRef\]](#)
60. Shang, Y.; Ding, Y.; Zhang, P.; Wang, M.; Jia, Y.; Xu, Y.; Li, Y.; Fan, K.; Sun, L. Pyrrolic N or pyridinic N: The active center of N-doped carbon for CO₂ reduction. *Chin. J. Catal.* **2022**, *43*, 2405–2413. [\[CrossRef\]](#)
61. Li, C.; Wang, Y.; Xiao, N.; Li, H.; Ji, Y.; Guo, Z.; Liu, C.; Qiu, J. Nitrogen-doped porous carbon from coal for high efficiency CO₂ electrocatalytic reduction. *Carbon* **2019**, *151*, 46–52. [\[CrossRef\]](#)
62. Sun, J.; Ge, Q.; Guo, L.; Yang, Z. Nitrogen doped carbon fibers derived from carbonization of electrospun polyacrylonitrile as efficient metal-free HER electrocatalyst. *Int. J. Hydrogen Energy* **2020**, *45*, 4035–4042. [\[CrossRef\]](#)
63. Verma, J.; Goel, S. Cost-Effective Electrocatalysts for hydrogen evolution reactions (HER): Challenges and prospects. *Int. J. Hydrogen Energy* **2022**, *47*, 38964–38982. [\[CrossRef\]](#)
64. Cordero-Lanzac, T.; Rosas, J.M.; García-Mateos, F.J.; Ternero-Hidalgo, J.J.; Palomo, J.; Rodríguez-Mirasol, J.; Cordero, T. Role of different nitrogen functionalities on the electrochemical performance of activated carbons. *Carbon* **2018**, *126*, 65–76. [\[CrossRef\]](#)

65. Fan, Y.; Yi, Z.; Zhou, Y.; Xie, L.; Sun, G.; Wang, Z.; Huang, X.; Su, F.; Chen, C. The relationship between the high-frequency performance of supercapacitors and the type of doped nitrogen in the carbon electrode. *New Carbon Mater.* **2024**, *39*, 1015–1026. [\[CrossRef\]](#)
66. Yadav, A.; Kumar, R.; Joseph, D.; Thomas, N.; Yan, F.; Sahoo, B. Impact of dispersive solvent and temperature on supercapacitor performance of N-doped reduced graphene oxide. *C* **2024**, *10*, 89. [\[CrossRef\]](#)
67. Hasegawa, G.; Deguchi, T.; Kanamori, K.; Kobayashi, Y.; Kageyama, H.; Abe, T.; Nakanishi, K. High-level doping of nitrogen, phosphorus, and sulfur into activated carbon monoliths and their electrochemical capacitances. *Chem. Mater.* **2015**, *27*, 4703–4712. [\[CrossRef\]](#)
68. Zhai, Y.; Xu, B.; Zhu, Y.; Qing, R.; Peng, C.; Wang, T.; Li, C.; Zeng, G. Nitrogen-doped porous carbon from camellia oleifera shells with enhanced electrochemical performance. *Mater. Sci. Eng. C* **2016**, *61*, 449–456. [\[CrossRef\]](#) [\[PubMed\]](#)
69. Zhang, Y.; Zhang, Y.; Huang, J.; Du, D.; Xing, W.; Yan, Z. Enhanced capacitive performance of N-doped activated carbon from petroleum coke by combining ammoxidation with KOH activation. *Nanoscale Res. Lett.* **2016**, *11*, 245. [\[CrossRef\]](#)
70. Rashidi, N.A.; Yusup, S. Recent methodological trends in nitrogen-functionalized activated carbon production towards the gravimetric capacitance: A mini review. *J. Energy Storage* **2020**, *32*, 101757. [\[CrossRef\]](#)
71. Han, W.; Wang, H.; Xia, K.; Chen, S.; Yan, P.; Deng, T.; Zhu, W. Superior nitrogen-doped activated carbon materials for water cleaning and energy storing prepared from renewable leather wastes. *Environ. Int.* **2020**, *142*, 105846. [\[CrossRef\]](#)
72. Arango, D.I.; Zapata-Benabith, Z.; Arenas, E.C.; Perez-Osorno, J.C. Influence of surface modification with nitric acid on electrochemical performance of agroindustrial waste-based activated carbon. *J. Mater. Sci. Mater. Electron.* **2018**, *29*, 15557–15569. [\[CrossRef\]](#)
73. Shaker, M.; Ghazvini, A.A.S.; Shahalizade, T.; Gaho, M.A.; Mumtaz, A.; Javanmardi, S.; Riahiyar, R.; Meng, X.; Jin, Z.; Ge, Q. A review of nitrogen-doped carbon materials for lithium-ion battery anodes. *New Carbon Mater.* **2023**, *38*, 247–278. [\[CrossRef\]](#)
74. Yuan, R.; Hou, R.; Shang, L.; Liu, X.; Li, A.; Chen, X.; Song, H. The preparation and properties of N-doped carbon materials and their use for sodium storage. *New Carbon Mater.* **2024**, *39*, 770–795. [\[CrossRef\]](#)
75. Feng, S.; dos Santos, M.C.; Carvalho, B.R.; Lv, R.; Li, Q.; Fujisawa, K.; Elías, A.L.; Lei, Y.; Perea-López, N.; Endo, M.; et al. Ultrasensitive molecular sensor using N-doped graphene through enhanced raman scattering. *Sci. Adv.* **2016**, *2*, e1600322. [\[CrossRef\]](#)
76. Lawaniya, S.D.; Kumar, S.; Yu, Y.; Awasthi, K. Nitrogen-doped carbon nano-onions/polypyrrole nanocomposite based low-cost flexible sensor for room temperature ammonia detection. *Sci. Rep.* **2024**, *14*, 7904. [\[CrossRef\]](#)
77. Zhang, S.; Lan, D.; Zheng, J.; Kong, J.; Gu, J.; Feng, A.; Jia, Z.; Wu, G. Perspectives of nitrogen-doped carbons for electromagnetic wave absorption. *Carbon* **2024**, *221*, 118925. [\[CrossRef\]](#)
78. Zhang, X.; Zhao, Z.; Xu, J.; Ouyang, Q.; Zhu, C.; Zhang, X.; Zhang, X.; Chen, Y. N-doped carbon nanotube arrays on reduced graphene oxide as multifunctional materials for energy devices and absorption of electromagnetic wave. *Carbon* **2021**, *177*, 216–225. [\[CrossRef\]](#)
79. Bianco, G.V.; Sacchetti, A.; Grande, M.; D’Orazio, A.; Milella, A.; Bruno, G. Effective Hole Conductivity in nitrogen-doped CVD-graphene by singlet oxygen treatment under photoactivation conditions. *Sci. Rep.* **2022**, *12*, 8703. [\[CrossRef\]](#)
80. Ortega, K.F.; Arrigo, R.; Frank, B.; Schlögl, R.; Trunschke, A. Acid–base properties of N-doped carbon nanotubes: A combined temperature-programmed desorption, x-ray photoelectron spectroscopy, and 2-propanol reaction investigation. *Chem. Mater.* **2016**, *28*, 6826–6839. [\[CrossRef\]](#)
81. Kundu, S.; Xia, W.; Busser, W.; Becker, M.; Schmidt, D.A.; Havenith, M.; Muhler, M. The formation of nitrogen-containing functional groups on carbon nanotube surfaces: A quantitative XPS and TPD study. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4351. [\[CrossRef\]](#) [\[PubMed\]](#)
82. Zhai, Y.; Pang, D.; Chen, H.; Xiang, B.; Chen, J.; Li, C.; Zeng, G.; Qiu, L. Effects of ammonization on the surface physico-chemical properties of sludge-based activated carbon. *Appl. Surf. Sci.* **2013**, *280*, 590–597. [\[CrossRef\]](#)
83. Jansen, R.J.J.; van Bekkum, H. XPS of nitrogen-containing functional groups on activated carbon. *Carbon* **1995**, *33*, 1021–1027. [\[CrossRef\]](#)
84. Mainali, K.; Mood, S.H.; Pelaez-Samaniego, M.R.; Sierra-Jimenez, V.; Garcia-Perez, M. Production and applications of N-doped carbons from bioresources: A review. *Catal. Today* **2023**, *423*, 114248. [\[CrossRef\]](#)
85. Boehm, H. Surface oxides on carbon and their analysis: A critical assessment. *Carbon* **2002**, *40*, 145–149. [\[CrossRef\]](#)
86. 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. [\[CrossRef\]](#)
87. Prauchner, M.J.; Rodríguez-Reinoso, F. Chemical versus physical activation of coconut shell: A comparative study. *Microporous Mesoporous Mater.* **2012**, *152*, 163–171. [\[CrossRef\]](#)
88. Biesinger, M.C. Accessing the robustness of adventitious carbon for charge referencing (correction) purposes in XPS analysis: Insights from a multi-user facility data review. *Appl. Surf. Sci.* **2022**, *597*, 153681. [\[CrossRef\]](#)

89. Biesinger, M.C. X-Ray Photoelectron Spectroscopy (XPS) Reference Pages—Label Oxygen. Available online: <https://www.xpsfitting.com/search/label/Oxygen> (accessed on 22 December 2024).
90. Beamson, G.; Briggs, D. High resolution XPS of organic polymers: The Scienta ESCA300 Database. *J. Chem. Educ.* **1993**, *70*, A25.
91. Herold, F.; Gläsel, J.; Etzold, B.J.M.; Rønning, M. Can temperature-programmed techniques provide the gold standard for carbon surface characterization? *Chem. Mater.* **2022**, *34*, 8490–8516. [[CrossRef](#)]
92. Li, N.; Ma, X.; Zha, Q.; Kim, K.; Chen, Y.; Song, C. Maximizing the number of oxygen-containing functional groups on activated carbon by using ammonium persulfate and improving the temperature-programmed desorption characterization of carbon surface chemistry. *Carbon* **2011**, *49*, 5002–5013. [[CrossRef](#)]
93. Razdyakonova, G.I.; Kokhanovskaya, O.A.; Likholobov, V.A. Influence of environmental conditions on carbon black oxidation by reactive oxygen intermediates. *Procedia Eng.* **2015**, *113*, 43–50. [[CrossRef](#)]
94. Ishii, T.; Ozaki, J. Understanding the chemical structure of carbon edge sites by using deuterium-labeled temperature-programmed desorption technique. *Carbon* **2020**, *161*, 343–349. [[CrossRef](#)]
95. Vottero, E.; Carosso, M.; Pellegrini, R.; Piovano, A.; Groppo, E. Assessing the functional groups in activated carbons through a multi-technique approach. *Catal. Sci. Technol.* **2022**, *12*, 1271–1288. [[CrossRef](#)]
96. Hall, P.J.; Calo, J.M. Secondary interactions upon thermal desorption of surface oxides from coal chars. *Energy Fuels* **1989**, *3*, 370–376. [[CrossRef](#)]
97. Düngen, P.; Schlögl, R.; Heumann, S. Non-linear thermogravimetric mass spectrometry of carbon materials providing direct speciation separation of oxygen functional groups. *Carbon* **2018**, *130*, 614–622. [[CrossRef](#)]
98. Vivo-Vilches, J.F.; Bailón-García, E.; Pérez-Cadenas, A.F.; Carrasco-Marín, F.; Maldonado-Hódar, F.J. Tailoring the surface chemistry and porosity of activated carbons: Evidence of reorganization and mobility of oxygenated surface groups. *Carbon* **2014**, *68*, 520–530. [[CrossRef](#)]
99. Cândido, N.R.; Prauchner, M.J.; Vilela, A.D.O.; Pasa, V.M.D. The use of gases generated from eucalyptus carbonization as activating agent to produce activated carbon: An integrated process. *J. Environ. Chem. Eng.* **2020**, *8*, 103925. [[CrossRef](#)]
100. Rodríguez-Reinoso, F.; Molina-Sabio, M. Textural and chemical characterization of microporous carbons. *Adv. Colloid Interface Sci.* **1998**, *76–77*, 271–294. [[CrossRef](#)]
101. Menendez, J.A.; Phillips, J.; Xia, B.; Radovic, L.R. On the modification and characterization of chemical surface properties of activated carbon: In the search of carbons with stable basic properties. *Langmuir* **1996**, *12*, 4404–4410. [[CrossRef](#)]
102. Prauchner, M.J.; Sapag, K.; Rodríguez-Reinoso, F. Tailoring biomass-based activated carbon for CH₄ storage by combining chemical activation with H₃PO₄ or ZnCl₂ and physical activation with CO₂. *Carbon* **2016**, *110*, 138–147. [[CrossRef](#)]
103. Prauchner, M.J.; Oliveira, S.D.C.; Rodríguez-Reinoso, F. Tailoring low-cost granular activated carbons intended for CO₂ adsorption. *Front. Chem.* **2020**, *8*, 581133. [[CrossRef](#)] [[PubMed](#)]
104. Pan, D.; Li, G.; Su, Y.; Wei, H.; Luo, Z. Kinetic study for the oxidation of cyclohexanol and cyclohexanone with nitric acid to adipic acid. *Chin. J. Chem. Eng.* **2021**, *29*, 183–189. [[CrossRef](#)]
105. Soudani, N.; Souissi-najar, S.; Ouederni, A. Influence of nitric acid concentration on characteristics of olive stone based activated carbon. *Chin. J. Chem. Eng.* **2013**, *21*, 1425–1430. [[CrossRef](#)]
106. Stöhr, B.; Boehm, H.P.; Schlögl, R. Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate. *Carbon* **1991**, *29*, 707–720. [[CrossRef](#)]
107. Marchon, B.; Tysoe, W.T.; Carrazza, J.; Heinemann, H.; Somorjai, G.A. Reactive and kinetic properties of carbon monoxide and carbon dioxide on a graphite surface. *J. Phys. Chem.* **1988**, *92*, 5744–5749. [[CrossRef](#)]

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